EVALUATION OF NANO ZEOLITE AS AN ADDITIVE FOR OIL-WELL CEMENTING

BY

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A Thesis Presented to the

DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

PETROLEUM ENGINEERING

May 2017

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

DEANSHIP OF GRADUATE STUDIES

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Dedication

I dedicate my work to my parents and my family.

ACKNOWLEDGEMENTS

I begin with the name of Allah, the most beneficent, the most merciful. May Allah bestow peace on our beloved Prophet Mohammed (*peace and blessings of Allah be upon him*), his family, his noble companions, and all those who follow them with righteousness until the Day of Judgment. I would like to thank the Almighty who gave me strength, guidance and patience to complete this thesis. It is Allah's (SWT) blessing on me, He made this work easy for me.

I would like to dedicate this thesis to my parents, without their prayers and support, I would not have been able to complete this research. I will never be able to thank them enough for whatever they have done for me. Their happiness will always remain my motivation to achieve big in my life. May Allah have mercy on them as they had mercy upon me when I was small. Special thanks to my siblings for their love, care and prayers. I am grateful to my family members in Karachi and Riyadh who always remembered me in their prayers.

Acknowledgements are due to *King Fahd University of Petroleum and Minerals* which gave me the opportunity to pursue a graduate degree through scholarship. I would like to thank Petroleum engineering department for providing the best environment which helped me grow professionally and the chairman, Dr Abdullah sultan, for all the support I received in carrying out this research.

I would like to express my deepest gratitude to my thesis advisor, Dr. Abdulaziz Al-Majed, my thesis Co-Advisor Dr. Kalimur Rahman, committee members Dr. Abdulazeez Abdulraheem, Dr. Salaheldin Elkatatny and Dr. Rahul Narayanrao Gajbhiye. I especially acknowledge Dr. Kalimur Rahman for his excellent guidance, unconditional support and ideas which helped me in completion of this thesis. I would like to thank Dr Al-Majed as well for his kind support.

I would also like to acknowledge Halliburton Dhahran technology center for allowing me to conduct experiments in the cementing lab and for providing the chemicals to complete this research. Special thanks to Dr Hicham El Hajj, Waseem Razzaq, Muzammil Shakeel and Tarek Moselhi for their support throughout the study.

I would also like to thank technical staff both from Halliburton and KFUPM who helped me throughout the thesis. Special thanks to Mr. Abdul Samad for his constant support throughout this period, not only professionally, but personally as well.

I am also grateful to all my colleagues, friends and seniors at KFUPM for providing the moral support and a pleasant atmosphere. Special thanks to friends Rizwan Ahmed Khan, Shams Kalam, Mobeen Murtaza, Waqas Ahmed Khan, Ahmed Mahboob, Danish Hashmat, Mir Mansoor Alam, Sarmad Sherwani, Zaid Zaffar, Hasan Sheikh and Mohammed Ali Al-Malki.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT (ENGLISH)

NAME: Mirza Talha Baig

TITLE: Evaluation of Nano zeolite as an Additive for Oil-Well Cementing

MAJOR FIELD: Petroleum Engineering

DATE OF DEGREE: May, 2017

Nanotechnology has provided a wide variety of solutions to resolve industry problems which could not be previously addressed by customary methods. It enables the researchers to alter properties of bulk materials at nanometer scale. Various nanomaterials have been successfully applied in many areas of petroleum engineering especially in drilling fluids, loss circulation, EOR and cementing. During the last decade, several nanomaterials such as Nano silica, Nano clays, Carbon nanotubes, Nano alumina, Nano ferrite and Nano titania have been explored in cementing applications. The primary focus of this study is to examine the performance of Oil-well cement with Nano zeolite as an additive. The performance of micro zeolite as compared to Nano zeolite is also presented.

In this thesis, the influence of addition of Nano zeolite and micro zeolite on oil well cement at high pressure and high temperature (HPHT) was examined. Nano zeolite was added in different percentages to the neat cement slurry and cement slurry mixture

presently used for oil/gas well cementing in Saudi Arabia. Experimental study addressed different cement slurry properties such as thickening time, free water separation, rheological properties, compressive strength, tensile strength, density, fluid loss, SEM, XRD and porosity & permeability.

Rheological properties like plastic viscosity, yield point and gel strength were increased with the addition of Nano zeolite. Hydration products were modified with the addition of Nano zeolite as indicated by SEM. Nano zeolite retarded the thickening time of cement slurry, while, micro zeolite acted as an accelerator. No significant effect of Nano and micro zeolite on density of cement slurry. Compressive strength was accelerated with both Nano and micro zeolite. Porosity and permeability was reduced significantly with Nano zeolite and denser microstructure was observed with SEM. Destructive compressive strength and tensile strength was shown to be increased with Nano zeolite addition. No significant effect on fluid loss of cement slurries with Nano zeolite.

Nano zeolite can serve as an effective additive for Oil-well cement as it enhances early compressive strength with improvement in durability properties of cement. Acceleration of compressive strength development will help in reducing wait-on cement time which will reduce operations cost. The enhancement of both compressive and tensile strength is particularly important for HPHT wells because of the many stresses to which they are subjected over the life of the well. While, denser microstructure may help to restrain the invasion of corrosive formation fluids.

ABSTRACT (ARABIC)

ملخص الرسالة

الاسم: **ميرزا طلحة بيج**

عنوان الرسالة: **تقييم الزيوليت المتناهي الصغركمادة إضافية لإسمنت أبار النفط**

التخصص: **هندسة البترول**

تاريخ التخرج: **مايو 2017م**

إن التقنيات متناهية الصغر أسهمت بمدى واسع من الحلول لمواجهة مشاكل الصناعة التي لا يمكن حلها بواسطة الطرق التقليدية. بهذه التقنيات أستطاع الباحثون تغيير خواص المواد السائبة بمقياس متناهي الصغير "نانومتري". استخدمت العديد من المواد المتناهية الصغر بنجاح في مجالات هندسة النفط خصوصاً في موائع الحفر، موائع لمنع فقدان دورة سائل الحفر، الإنتاج المحفز للنفط وسمنتة أبار النفط. خلال العقد المنصرم، استخدمت العديد من المواد المنتاهية الصغر في تطبيقات عملية سمنتة أبار النفط كالسيليكا المتناهية الصغر، الطفل المتناهي الصغر، الأنابيب الكربونية المتناهية الصغر، الأمونيا المتناهية الصغر، الفيريت المتناهية والتيتانيا المتناهية الصغر. إن الهدف الأساسي من هذه الدراسة هو الكشف عن أداء اسمنت النفط باستخدام الزيوليت المتناهي الصغر كمادة إضافية تضاف للإسمنت. تم أيضاً دراسة أداء إضافة الزيوليت الصغير (الميكروي) للإسمنت ومقارنتها مع الزيوليت المتناهي الصغر.

في هذه الرسالة، سندرس تأثير إضافة الزيوليت الصغير والزيوليت المتناهي الصغر في إسمنت أبارالنفط تحت ظروف الضغط ودرجة الحرارة العالتين (HPHT). هذا الزيولايت المتناهي الصغرستضاف بنسب بمختلفة لخليط

الإسمنت المستخدم حالياً في عملية سمنتة أبار النفط والغاز في المملكة العربية السعودية. أجريت دراسات مخبرية لمعرفة خصائص خليط الإسمنت كزمن التثخين، خاصية فصل الماء الحر، الخواص الريولوجية (الخواص المتعلقة بتشوه المادة)، القوة الإنضغاطية، قوة الشد، الكثافة، خاصية فقدان السائل، دراسة المجهر الإلكتروني الماسح (SEM)، دراسة البلورات بالأشعة السينية (XRD)، المسامية والنفاذية.

وجد أن الخواص الريولوجية مثل اللزوجة البلاستيكية ونقطة الخضوع وقوة الجل تزيج بإضافة الزيوليت المتناهي الصغر. منتجات عملية التميه تغيرت بإضافة الزيوليت المتناهي الصغر كما هو ملاحظ في دراسات المجهر الإلكتروني الماسح (SEM). وجد أن الزيوليت المتناهي الصغر يؤخر زمن تخثين خليط الإسمنت بينما الزيوليت الصغير يعمل كمادة مسرعة للتثخين. لم يلاحظ تغير مهم في كثافة الإسمنت عند إضافة الزيوليت المتناهي الصغر بينما وجد أن القوة الإنضغاطية تزداد بسرعة عند إضافة الزيوليت الصغير والزيوليت المتناهي الصغر. وجد أن الزيوليت المتناهي الصغر يعمل على تقليل مسامية ونفاذية الإسمنت وبالتالي الحصول على إنشاء مجهري كثيف للإسمنت عند ملاحظته في دراسة المجهر الإلكتروني الماسح (SEM). وجد أن القوة الإنضغاطية بواسطة عملية التحطيم تزداد بإضافة الزيوليت المتناهي الصغر للإسمنت بينما لم يلاحظ تغير مهم في خاصية فقدان السائل للإسمنت عند إضافة الزيوليت المتناهي الصغر.

يعمل الزيوليت المتناهي الصغر كمادة إضافية فعّالة لإسمنت أبار النفط لأنها تحسن القوة الإنضغاطية المبكرة وبالإضافة إلى تحسين متانة الإسمنت. تسريع القوة الإنضغاطية قد يساعد في تقليل زمن الإنتظار لتثخين الإسمنت وبالتالي يؤدي إلى تقليل التكلفة التشغيلية لحفر الأبار. إن عملية تحسين القوة الإنضغاطية وقوة الشد مهمة عملياً للأبار ذات الضغط ودرجة الحرارة العاليتين (HPHT) بسبب قوات الشد العالية التي تتعرض لها هذه الأبار في طوال حياتها بينما يساعد الإنشاء المجهري الكثيف للإسمنت في تحسين خاصية مقاومة السوائل المتآكلة الموجودة في الطبقات الأرضية.

CHAPTER 1

INTRODUCTION

1.1 OVERVIEW

Oil and gas production and its exploration have an ultimate influence on the world's economic structure. The conventional petroleum reservoirs are exhausting because of increase in economic activity in last decades. To bridge the gap between supply and demand of petroleum products, engineers are now exploring the reserves, which were neglected in past due to various complications associated. Technological advancements in the field of petroleum engineering now enable researchers to cope with the problems efficiently and improve the overall success of operations. To exploit the unconventional resources, new techniques must be established simultaneously with the improvement in the existing techniques.

The Kingdom of Saudi Arabia has 266.455 billion barrels of proven crude oil reserves and it has the fourth largest global gas reserves of 303 trillion cubic feet. In 2015, crude oil production of Saudi Arabia was approximately 10.19 million barrels/day, and 145 rigs were active. Saudi Arabia completed 616 wells in 2015 as compared to 538 in 2014

(OPEC Annual Statistical Bulletin 2016). With the successful application of modern technology in USA for unconventional reservoirs, other countries including Saudi Arabia are also looking to intensify their efforts for exploration and production from unconventional resources.

Performance of a drilled well in terms of production is dependent on a successful cementing job, which prevents any fluid migration in the well, provides a good seal between the formation and casing, protects casing from corrosion and provides support to it (Calvert and Smith, 1990). Primary cementing job must be performed to ensure that the above-mentioned goals are accomplished without the need of costly remedial cementing job (Sauer and Landrum, 1985).

Successful drilling job requires not only reaching the reservoir target economically but also provide safe conduit for the reservoir fluids to flow for lifetime of well. A good well design involves securing shallow water zones as well as restricting any inflow of fluid, which can result in increase of casing pressure. Well cement serves the purpose of supporting the casing as well as mitigating any communication of formation fluids from the wellbore.

Zonal isolation is by far one of the most significant functions of the cement job as flowing fluids from annulus can result in well control issues. For production wells, ineffective zonal isolation can result in loss of reservoir fluids to other formations or invasion of fluids from other formations. In injectors, injected fluid might be lost to other layers because of improper hydraulic seal by cement. It can also result in improper

hydraulic fracturing job because of the fracturing fluid loss (Economides, 1990). Zonal isolation specifically becomes more challenging in HPHT formations because of cyclic loads and temperature cycles, which can affect integrity of cement sheath negatively.

API recommended practice 65-2 (2010) summarized some of the key considerations for designing cementing job for isolating flow potential zone. Evaluation of flow zones is necessary to design cement slurry according to the flow potential of individual zones. Pore pressure and fracture gradient is critical for designing any cementing job so that problems like lost circulation and annular flows can be avoided. Accurate estimation of downhole temperature both circulating and static is required for any successful cementing job as cement properties are mainly dependent on temperature. Effective removal of drilling fluid from the well prior to cementing job is another contributing factor. Spacer and cement slurries must be designed considering the drilling fluid present in the well. Cement slurry designed must be tested in laboratory ahead of the cementing job at the downhole pressure and temperature conditions. Cement performance requirement parameters as present in API RP 65-2 are summarized below:

a) Rheological properties
b) Hydrostatic pressure control
c) Fluid loss control
d) Free fluid and sedimentation control
e) Static gel strength development
f) Resistance to invasion of gas or fluid

g) Compressive or sonic strength development

h) Shrinkage/expansion

i) Long-term cement sheath integrity

This must be noted that these requirements may vary for every job depending on the well objectives and conditions.

High Pressure High Temperature (HPHT) and deeper wells require cement slurry to be designed carefully as the cementing job becomes more challenging because high temperature and pressure affects both physical and chemical behavior of the cement materials in an undesirable manner. This difficult situation creates several challenges both during the well cementing operations while pumping and along the lifetime of well when the cement is set (Shadravan and Amani, 2012). Issues like strength retrogression and gas migration make cementing job in HPHT environment a challenging task, which requires more studies to improve the performance of existing slurries. Nanotechnology can suggest a variety of solutions to resolve many industry problems that may not be resolved by customary methods (Li et al., 2013).

To the extent of current knowledge, no literature describing application of Nano zeolite to improve properties of cement slurry systems for oilfield application has been documented. The objective of this study is to evaluate Nano zeolite as an additive for improving the properties of cement. The core emphasis of this research is to document the effects of Nano zeolite material on various cement properties. A typical Middle East

well is selected to study the cement mixture design and the effect of Nano zeolite is analyzed on several cement parameters in different concentrations.

1.2 ZEOLITE AND ITS NANO PARTICLES

Zeolites are porous alumino-silicate minerals that may be either natural or synthetic. Synthetic zeolites are created on the same structure as the natural zeolites are based on and are composed of alumino-silicate hydrates possessing the basic formula as presented below:

$$M_{a/n}[(AlO_2)_2(SiO_2)_b].xH_2O$$

Where M represents cations; n represents the cation valence; and x represents the moles of water incorporated into the zeolite structure (Luke et al., 2004).

Zeolites are three dimensional, micro porous crystalline solids with well-defined structures. It encompasses void spaces in its structure that can hold water, cations or other molecules. Molecular structures of different kind of zeolites are shown in **Figure 1-1**.

Natural zeolites are excellent pozzolanic materials. Its higher external surface area and metastability is believed to be the cause of its reactivity, which complement the formation of calcium silicate and aluminate hydrates (CSH and CAH) after the reaction with calcium hydroxide (Caputo et al., 2008).

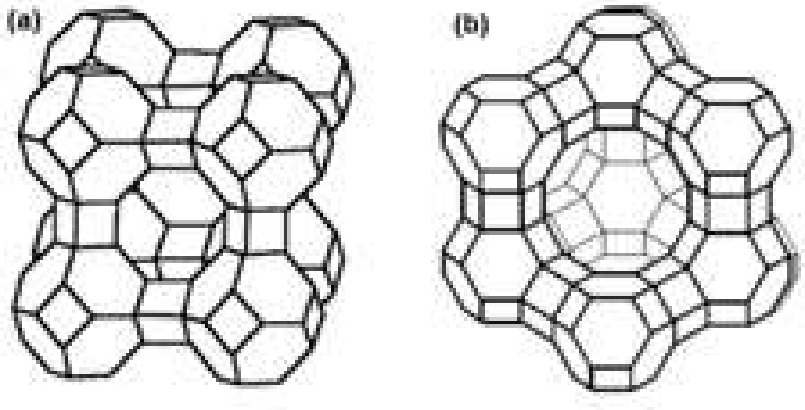

Figure 1-1: (a) Zeolite A (b) Zeolite X (Caputo et al., 2008).

Properties of the materials are significantly changed as particle size is decreased to nanometer, which results in improved performance as compared to their micro counterpart. Nanoparticles of zeolite have high surface area, which results in higher surface activity (Tosheva & Valtchev, 2005).

As nanoparticles are more reactive, they can be toxic and hazardous for human health even if same material in micro size was not toxic. Therefore, safety and toxicity analysis should be performed for Nano zeolite particles. However, Mintova et al., 2013 reported nano-sized zeolites show no or very low toxicity to the HeLa cells.

1.3 NEED FOR THIS RESEARCH

One of the challenges in successful drilling job is to provide good zonal isolation for the life of the well. Exploration of hydrocarbons in unacquainted areas required more cost-effective solutions to the cementing problems. These problems become worse in deeper

wells, so research is needed to test new additives that can improve cement slurries for challenging wells.

Nanotechnology with its numerous applications in various fields has prompted the interest of researchers to use it for benefits of petroleum industry. There are limited numbers of studies present currently on the use of nanomaterials for Oil-well cementing applications. Studies are required to evaluate the potential of nanomaterials as prospective admixtures for enhancement in cement properties.

1.4 PROBLEM STATEMENT

The application of nanotechnology to oil and gas industry is rapidly becoming an important area for research and development. This research aims to analyze the effects of Nano zeolite as an additive for oil cement systems. Currently no literature study is available explaining the application of Nano zeolite in cementing industry.

Cement slurry is analyzed for various properties such as rheology, density, thickening time, free fluid, fluid loss, compressive strength development with time, tensile strength before it is pumped in well. This research will examine the effects of Nano zeolite on Oil-well cement slurry using API Class-G cement with other additives as well as without any additives. Micro zeolite will also be tested to compare its effect with Nano zeolite.

1.5 THESIS OBJECTIVES

The main objective of this research was to study various properties of Oil-well cement (OWC) with Nano zeolite as an additive. API Class G cement was used for the research work as it is commonly used for most type of cement jobs with addition of various admixtures. Experimental investigation was performed to demonstrate the effects of Nano zeolite on OWC properties.

This study also attempted to understand various challenges for cementing zones like HPHT, and way in which application of nanotechnology might help in resolving some of the challenges. Performance of Nano zeolite at severe temperature and pressure conditions was analyzed that can be useful for successful cementing job in difficult areas. The outcomes of this study could help in designing optimum mixture design with Nano zeolite as an additive.

The following properties of OWC slurry with Nano zeolite were studied:

a) Thickening time
b) Free water separation
c) Rheology
d) Compressive strength
e) Tensile strength
f) Density
g) Static fluid loss

h) Porosity and permeability

i) XRD and SEM analysis

1.6 THESIS ORGANIZATION

This thesis has been prepared as per the guidelines stated by the Deanship of Graduate Studies of King Fahd University of Petroleum & Minerals. It has been divided into six chapters as follows:

Chapter 1 covers the background and introduction of the current thesis. The objectives of current thesis are also discussed in this chapter.

Chapter 2 explains the literature study, which covers the basics of cement, different kind of cement additives and factors affecting cement design. It presents some of the work previously done in Oil well cementing and different nanomaterials used in cementing industry.

Chapter 3 presents the methodology and experimental program of the research work along with the temperature and pressure conditions used. It explains in detail how each cement property is evaluated as per the specifications of API.

Chapter 4 discusses the results of all experimental tests conducted to analyze the behavior of neat cement slurry with Nano zeolite in the absence of other additives.

Chapter 5 discusses the results of all experimental tests conducted to analyze the behavior of cement slurry with Nano zeolite and micro zeolite in the presence of other additives.

Chapter 6 concludes the work with the major research outcomes and furnished recommendations for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

Oil well cementing involves the process of placing the cement slurry through casing to the annulus between casing and formations. Usually cement slurry is preceded by spacers to flush the already present drilling fluid from the hole and annulus. Although specific objectives for any specific job may be different but generally these are the main objectives of Oil well cementing (Hossain & Al-Majed, 2015 and Al-Yami, 2015):

- Effective zonal isolation to avoid any fluid migration in the annulus
- To support the walls of the wellbore to prevent formation collapse
- To prevent movement of gas or fluids between different geological formations
- To protect oil producing zones from salt water flow
- To support and seal the casing in place and protect it from collapse under pressure
- To protect well casings from corrosion

- To reduce the risk of ground water contamination by oil, gas or salt water
- To seal lost circulation zones

Portland cements used in construction industry cannot be used for oil/gas wells as Oil-well cements are exposed to wide range of temperature and pressure and stresses over the life of well. Hence, Portland cements are modified for use as Oil-well cement with a variety of cement additives present to modify the cement properties according the performance requirement. Cement should remain pumpable for the placement time at deeper depths, should develop enough strength at earlier times to reduce weight on cement time and remain durable for the lifetime of well (Nelson, 1990). American Petroleum Institute (API) has specified various chemical, physical and performance requirements for different classes of cement to be used as Oil-well cement in API Specification 10A. The properties of cement can then further be modified by use of different additives to achieve required pumpability, mechanical properties and durability for life of well.

This chapter reviews the basic concepts of Oilwell cementing, cement hydration and design process. Moreover, it includes review of different classes of OWCs used in petroleum industry with their chemical and physical properties and understanding of the additives, which are currently being used to modify the cement properties for different job requirements. A concise summary of different nanomaterials and zeolite used in the literature for cementing applications is also presented.

2.2 WELL CEMENTING

When one well section has been drilled completely, casing is run to desired depth, which is then cemented to provide zonal isolation. The existing drilling fluid in hole is displaced through annulus by spacer then followed by cement slurry. After placement of cement in annulus, enough weight on cement (WOC) is given to the slurry to develop compressive strength. Hardened cement paste than work as effective barrier as permeability is reduced.

Generally, in primary cementing job cement is pumped through casing to fill the annulus. However, in some cases, “top up” technique is also used in which cement is directly pumped in annulus. Two types of cementing plug (top and bottom) are typically used on a cementing operation. Bottom plug displaces the drilling fluid out of casing while cleaning the casing walls of any fluid left, which is followed by cement slurry pumping. Top plug is then released which displaces cement slurry out of casing into the annulus. Top plug is displaced by drilling fluid or water, which then bump into bottom plug, sweeping any cement from the wall of casing. Sometimes, multiple stage cementing is also performed for example when cementing weaker formations, which cannot bear higher hydrostatic pressure, is cemented with lower density slurry. Rest of the open hole is then placed with higher density cement slurry (Burdylo & Birch, 1990 and Hossain & Al-Majed, 2015).

After the cementing process, a curing time is allowed for the slurry to harden before beginning completion work or drilling to a deeper horizon. The set cement slurry forms a low permeability annulus and isolates the productive zone of the well from the rest of the formation.

2.3 CLASSIFICATION OF OIL-WELL CEMENT

Portland cement is the most used type of cement as binding material. Cement used for oil/gas wells is subjected to more hostile conditions than the cement used in construction industry which is exposed to ambient temperature and pressure conditions. Portland cement thus had to be modified prior to its use as well cement. Portland cement is hydraulic cement, which set and hardened by the hydration reaction of water with cement. Well cement is exposed to variety of temperature, pressure and depth, so different classes of Portland cement are manufactured for different applications (Michaux et al, 1990).

Portland cement consists principally of four compounds: tricalcium silicate (Ca_3SiO_5) written in short as C_3S, dicalcium silicate (Ca_2SiO_4) written in short as C_2S, tricalcium aluminate written in short as C_3A and tetracalcium aluminoferrite written in short as C_4AF. A small amount of gypsum is also added to control hydration of C_3A which can cause flash set (Michaux et al, 1990 and Al-Yami, 2015).

Previously, testing procedure and specifications for well cements were based on ASTM standards. As ASTM standards were not established for the conditions that are generally

encountered in oil/gas wells, petroleum industry thought to establish its own standards. The first tentative standard in 1953, designated API Std. 10A, was entitled API Specification for Oil-Well Cements. The chemical and physical requirements for different classes of cement are determined per ASTM standards and modified for the use as well cement. These standards are modified annually to cater the needs of industry (Calvert & Smith, 1990).

These standards classify various classes of cements by defining the minimum requirements for each type of classes to be accepted. API standards classify 8 different classes of cement from A to H differentiated with respect to depths, pressures and temperatures conditions up to which they can be exposed. Class G and H are the most widely used classes of cements. In international operations, most of the well cement used is Class G (Canada, Europe, Middle East, South America, and Far East) (Calvert & Smith, 1990). Within these classes, three different grades are available with varying sulphate resistance, namely Ordinary (O), Moderate Sulphate Resistance (MSR) and High Sulphate Resistance (HSR), which is a function of amount of C_3A present in the cement (Michaux et al, 1990).

Chemical requirements of different type of cements, as described in API Specification 10A, are presented in **Table 2-1**.

Class B has lower C_3A, which makes it sulfate resistant. Class C has Higher C_3S, lower C_2S and high fineness which results in high early strength. Class D& E with higher C_2S and lower C_3S along with low fineness is termed as retarded cement designed for deep

wells. The most commonly used OWCs nowadays are API Class G and H. Only difference between these two is particle size, API Class G has smaller particle size, which gives it higher surface area. API class H has lower surface area that is why it has lower water requirement (Michaux et al, 1990).

Table 2-1: Chemical requirements for different classes of cement (API Specification 10A)

	Cement class					
	A	**B**	**C**	**D**	**G**	**H**
Ordinary grade (O)						
Magnesium oxide (MgO), maximum, percent	6,0	NA[a]	6,0	NA	NA	NA
Sulfur trioxide (SO_3), maximum, percent[b]	3,5	NA	4,5	NA	NA	NA
Loss on ignition, maximum, percent	3,0	NA	3,0	NA	NA	NA
Insoluble residue, maximum, percent	0,75	NA	0,75	NA	NA	NA
Tricalcium aluminate (C_3A), maximum, percent[d]	NR[c]	NA	15	NA	NA	NA
Moderate sulfate-resistant grade (MSR)						
Magnesium oxide (MgO), maximum, percent	NA	6,0	6,0	6,0	6,0	6,0
Sulfur trioxide (SO_3), maximum, percent[b]	NA	3,0	3,5	3,0	3,0	3,0
Loss on ignition, maximum, percent	NA	3,0	3,0	3,0	3,0	3,0
Insoluble residue, maximum, percent	NA	0,75	0,75	0,75	0,75	0,75
Tricalcium aluminate (C_3A), maximum, percent[d]	NA	NR	NR	NR	58	58
minimum, percent[d]	NA	NR	NR	NR	48	48
Tricalcium aluminate (C3A), maximum, percent[d]	NA	8	8	8	8	8
Total alkali content, expressed as sodium oxide (Na2O) equivalent, maximum, percent[e]	NA	NR	NR	NR	0,75	0,75
High sulfate-resistant grade (HSR)						
Magnesium oxide (MgO), maximum, percent	NA	6,0	6,0	6,0	6,0	6,0
Sulfur trioxide (SO_3), maximum, percent[b]	NA	3,0	3,5	3,0	3,0	3,0
Loss on ignition, maximum, percent	NA	3,0	3,0	3,0	3,0	3,0
Insoluble residue, maximum, percent	NA	0,75	0,75	0,75	0,75	0,75
Tricalcium aluminate (C_3A), maximum, percent[d]	NA	NR	NR	NR	65	65
minimum, percent[d]	NA	NR	NR	NR	48	48
Tricalcium aluminate (C3A), maximum, percent[d]	NA	3	3	3	3	3
Tetracalcium aluminoferrite (C4AF) plus twice the Tricalcium aluminate (C_3A), maximum, percent[d]	NA	24	24	24	24	24
Total alkali content, expressed as sodium oxide (Na2O) equivalent, maximum, percent[e]	NA	NR	NR	NR	0,75	0,75

Key properties of various classes of cement are summarized in **Table 2-2** and **Table 2-3**.

Table 2-2: Classes of oil-well cement (API Specification 10A, Michaux et al, 1990)

Cement Class	W/C Ratio	Range of depth (ft.)	Description
A	46	0 to 6000	Used when no special property is required, available only in Ordinary type
B	46	0 to 6000	Used when moderate to high sulfate resistance is required
C	56	0 to 6000	Used when high early strength is required, available in O, MSR and HSR grades
D	38	6000 to 10,000	For moderately high temperature and pressure, available in MSR & HSR grades
E	38	10,000 to 14,000	For high temperature and pressure, available in MSR & HSR grades
F	38	10,000 to 16,000	For extremely high temperature and pressure, available in MSR & HSR grades
G	44	0 to 8,000	Can be modified with use of accelerator and retarder, available in MSR & HSR grades
H	38	0 to 8,000	Can be modified with use of accelerator and retarder, available in MSR & HSR grades

Table 2-3: Typical properties of API oil-well cements (Michaux et al, 1990)

API Class	C_3S %	C_2S %	C_3A %	C_4AF %	Fineness cm2/g	Special Application
A	53	24	8	8	1500-1900	None
B	47	32	5	12	1500-1900	Sulfate resistant
C	58	16	8	8	2000-2800	Early setting
D&E	26	54	2	12	1200-1600	Retarded
G&H	50	30	5	12	1400-1700	More stringent specs.

2.4 OIL WELL CEMENT ADDITIVES

Cementing design can be modified as per the well requirements using different chemical additives available. As every cementing job is different, optimum number and concentration of additives must be selected as per the job requirement. No general guideline can be defined for selecting additives that is why cementing engineers should use field and lab experience while designing the slurry (Al-Yami, 2015).

Typical additives for OWC slurries can be categorized into following groups:

a) Accelerators

b) Retarders

c) Extenders

d) Weighting agents

e) Dispersants

f) Fluid-loss control agents

g) Lost circulation control agents

h) Antifoam agents

i) Anti-strength retrogression agents

The setting time of OWC can be controlled using retarder and accelerator. Weighting agents and extenders are used to control the density of the cement slurry. Likewise, dispersants or viscosifiers are added to control the viscosity of the slurry. Various fluid loss additives are available to control the fluid loss to the formations. A detailed review of cement additives has been provided by Nelson et al., 1990 and Michaux et al., 1990. Other than these additives, various pozzolan like silica fume, fly ash, zeolites have also been used as cement replacement.

Several properties of cement can be improved by use of single additive as Roshan and Asef (2010) demonstrated use of Carboxymethyl cellulose (CMC) as multifunctional additive for high early compressive strength, lower free fluid and less permeability.

2.4.1 Accelerators

Accelerators are used to accelerate the slurry thickening time. They are used for shallow casings or low temperature wells, where thickening time became very long. Longer thickening time may result in longer wait on cement (WOC) time, which will increase the rig time and cost of drilling. Accelerators does not affect the ultimate strength, they only expedite the development of strength. Calcium chloride is widely used in industry as an

accelerator because of efficiency and lower cost (Broni-Bediako et al, 2016). Mechanism of $CaCl_2$ acceleration is not completely understood. Pang et al., 2014 suggested that it increases cement hydration because of increase in Calcium concentration in the cement-pore solution.

2.4.2 Retarders

Retarders are used to increase thickening time, particularly in high temperature and deeper wells. As temperature accelerates the cement hydration, an effective retarder is required to counter the increased rate of hydration. Retarders only decrease the speed of strength development; ultimate strength will not be decreased. Retarding effect is sensitive to temperature, even a change of 5°C can affect thickening time significantly, so accurate prediction of Bottom Hole Circulating Temperature (BHCT) is explicitly important (Broni-Bediako et al, 2016). Lignosulphonates are the most commonly used retarder that are usually derived from wood pulp. Their mechanism of action is believed to be the adsorption on initial Calcium Silicate Hydrate (CSH) layer making it hydrophobic (Michaux et al., 1990).

2.4.3 Fluid Loss Agent

Fluid loss additives are added to minimize the filtrate loss from cement slurry to the permeable formation. Higher fluid loss tends to increase the effective density, change the rheology and increase the likelihood of annular gas migration. These additives reduce fluid loss by the formation of low permeability filter cake and/or increasing interstitial

water's viscosity. Fluid loss controlling agents are generally polymers, while cellulose derivatives are most commonly used (Michaux et al., 1990, Al-Yami, 2015 and Broni-Bediako et al, 2016).

2.4.4 Dispersants

Successful mud removal requires cement slurry to be pumped in turbulent flow. Dispersants enable cement slurry to achieve turbulent flow at lower pump rate to reduce the excessive friction pressures on pumps. Addition of dispersant also helps in reducing amount of water added, without increasing the viscosity of the slurry. Mostly cement dispersants are additives with anionic group. They create negatively charged particles on the surface of cement that repels other negatively charged particles, hence reducing the friction. The most commonly used dispersant is Polynapthalene sulfonate (Michaux et al., 1990, Al-Yami, 2015).

2.4.5 Anti-foaming Agents

Foaming in cement slurry while mixing is not desirable as it can cause damage to pump and entrapped air in slurry can give incorrect slurry density. Antifoaming agents are used to reduce foaming in cement and minimize any entrapped air. These additives work by modifying surface tension of slurry and typically very small quantity is required. Two types of anti-foam additives are generally used which are Polypropylene glycols and silicones (Broni-Bediako et al, 2016).

2.4.6 Extenders

Extenders are used to lower the density for weaker formations as higher density cement can cause formation to fracture, which will result in significant loss circulation. As extenders are cheaper than cement, they might reduce the overall cost if used as replacement of cement. The ultimate compressive strength is reduced significantly with the extenders. Three types of extenders are generally used which are water extenders, low-density aggregates and gas.

Bentonite is by far the mostly used water extenders. Pozzolans are most commonly used aggregates as they are siliceous and aluminous materials, which reacts with calcium hydroxide to increase the compressive strength simultaneously with decrease in density. Recently, microspheres are used as low density aggregate as they reduce density while preserving compressive strength. Nitrogen is used as a gas to prepare foamed cement slurry with very low density (Michaux et al., 1990 and Broni-Bediako et al, 2016).

2.4.7 Weighing Agent

When higher pore pressures, unstable formations and plastic formations are encountered, cement slurry density of more than 17.5 ppg may be required. Reducing water content may increase the density, but there is a practical limit as reducing too much water content may result in unpumpable slurry. So, these weighting additives are used to increase the density. Mostly used weighing materials are Hematite, Barite and Ilmenite (Broni-Bediako et al, 2016).

2.4.8 Lost Circulation Control Agents

Lost circulation can occur in zones while drilling fractured, vuggy and cavernous formations. These agents act as bridge material to plug the large fractures. Some of the lost circulation agents used are ground coal, ground gilsonite, ground walnut hull and cellophane flake (Michaux et al., 1990).

2.4.9 Expansion Additives

Cement slurries after placed in wellbore annulus may go through bulk shrinkage, which reduces external volume of cement after initial setting. This shrinkage even if not significant may affect bond properties of cement with pipe and formation that may be countered by the addition of expansive additives (Al-Yami, 2015 and Broni-Bediako et al, 2016).

2.4.10 Strength Retrogression Agents

At higher temperatures above 230°F (110°C), compressive strength started to decrease over time, which is termed as strength retrogression. Conversion of CSH gel to alpha-calcium di silicate hydrate (α-C2SH) is believed to be the reason of this retrogression as α-C2SH is crystalline and denser which cause shrinkage and thus increases the permeability. It can be decreased or prevented by adding alternative source of silica, such as silica flour or silica sand which will form a mineral called tobermorite (C5S6H5) having high strength and lower permeability (Al-Yami, 2015).

2.5 NANO MATERIALS

The advent of Nanotechnology opens new avenue of research, as Nanotechnology can be defined as the science of controlling the properties at nanometer scale, which can make revolutionary changes in bulk material properties. Using nanotechnology, the fundamental structure of materials can be modified to enhance the bulk materials properties. The difference of nanomaterials with normal micro sized materials comes down to structure and reactivity. Small particles have relatively more surface atoms looking to form bonds with their neighbors than large particles.

Petroleum researchers have been working hard to get the most out of Nanotechnology for the benefit of petroleum industry because of its considerable potential applications in the future. Various nanomaterials have been successfully applied in many areas especially in drilling fluids and cementing operations. A general overview of nanotechnology being used in drilling engineering is given in **Figure 2-1**.

Cement used in construction and petroleum industry has been improved with the use of Nano additives. Nanomaterials have shown the potential to improve compressive strength, tensile strength, microstructure, and durability properties without compromising other properties (Rae, 2008).

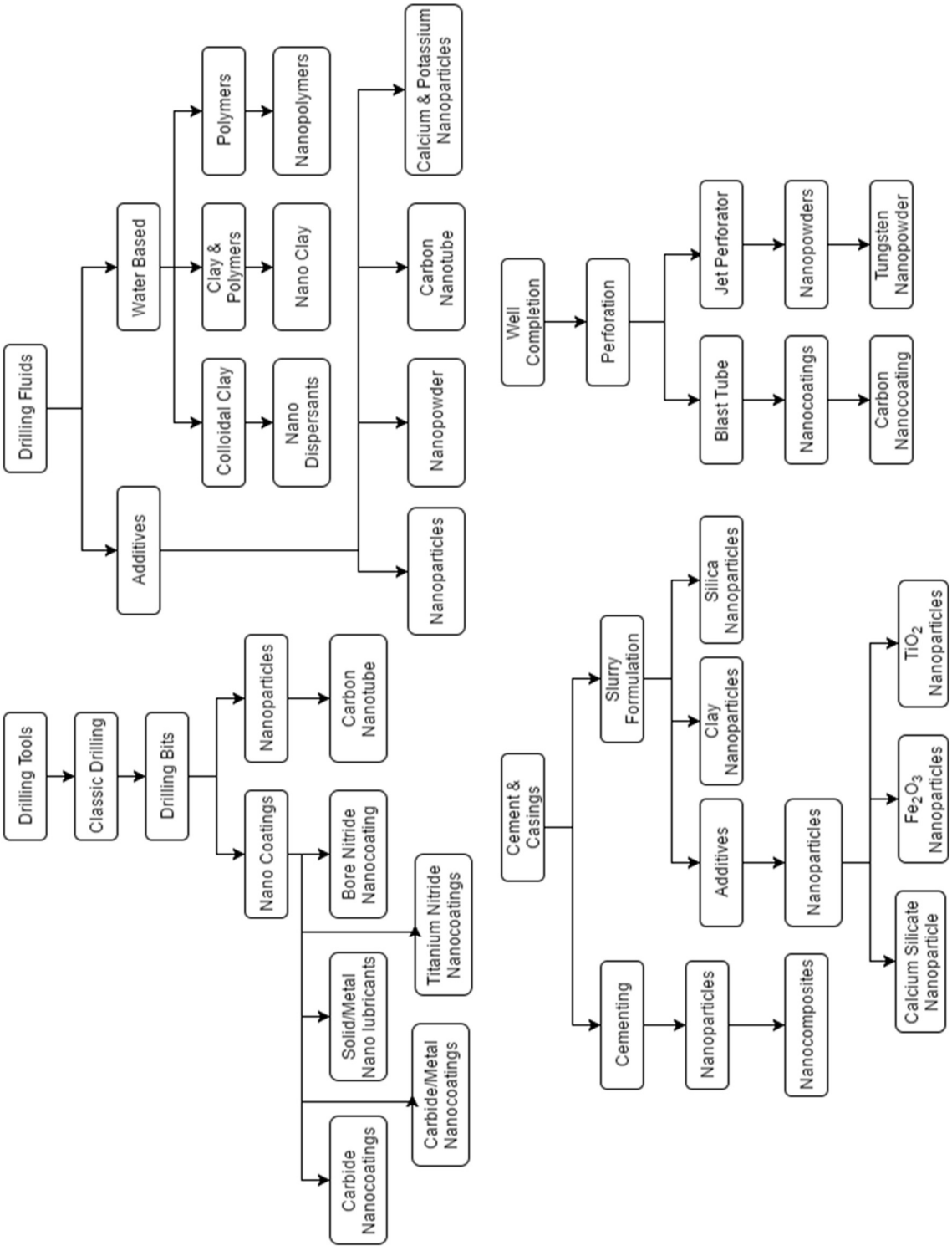

Figure 2-1: Applications of nanotechnology in drilling (Pourafshary et al., 2009)

Various types of Nano silica have been reported to increase compressive strength, enhance early compressive strength, reduce permeability and porosity, improve fluid loss, reduce transition time from 100lb/ft^2 to 500lb/ft^2 and decrease the density segregation (Ershadi et al. 2011; Patil and Deshpande 2012; Rahman et al. 2014). SEM images of cement mixes with Nanosilica confirmed nanofiller properties of Nanosilica for denser microstructure. Pang et al. 2014 observed that the improvement of properties with Nano silica is more prominent at lower density as more pore spaces are available for Nanosilica to provide nucleation sites for Calcium Silicate Hydrate (CSH) growth. Also, lower particle size and higher aspect ratios resulted in increased cement hydration which improved compressive strength.

Carbon nanotube has also been tested as an additive in Oil-well cementing to improve early compressive strength development, final compressive strength and tensile strength with very small concentration (dePaula et al/ 2014; Khan et al. 2016). Nanoclay has also been investigated as an admixture for oil-well cementing at HPHT (Murtaza et al. 2016). It was observed that Nano clay not only accelerated the early strength development but also increased the final strength along with reduction in permeability and porosity of hardened cement. Smaller particle size of Nanoclay aided in filling the capillaries and resulted in dense microstructure.

Different mechanisms that can contribute to the improved properties of cement paste by nanomaterials are explained below (He and Shi, 2008):

- They can act as nano-fillers that leads to denser and less permeable microstructure.
- They act as nucleation centers, contributing to the development of the hydration of Portland cement.
- Nano materials rich in silica react with $Ca(OH)_2$ crystals producing more C–S–H gel reducing the amount of $Ca(OH)_2$.

2.6 HYDRATION OF CEMENT SLURRIES

A typical composition of API class G cement is presented in

Table 2-4. Each of the compound experiences hydration when reacts with water. Only Silicates contribute to strength, which is almost 80% of total cement composition. C_3S is higher in quantity and it reacts much faster with water, so it contributes to the early compressive strength. C_2S is slower in reaction and hence it contributes to the final strength of the cement.

Calcium Silicate Hydrate, written as CSH gel in short form, formed in hydration reaction is an amorphous compound. About 70% of the fully hydrated cement at ambient conditions is CSH and it is considered as the main binder for the set cement. The C/S and H/S ratios are variable depending upon such factors as the calcium concentration in the aqueous phase, temperature, the presence of additives and aging. On the contrary, Calcium hydroxide (CH), which is called portlandite, is crystalline and hardened cement comprises of 15-20% of CH (Michaux et al, 1990).

Table 2-4: Composition of API Class G cement

Cement Compound	Symbols	Weight Percentage	Chemical Formula
Tricalcium silicate	C_3S	50	$3CaO.SiO_2$
Dicalcium silicate	C_2S	30	$2CaO.SiO_2$
Tricalcium aluminate	C_3A	5	$3CaO.Al_2O_3$
Tetracalcium aluminoferrite	C_4AF	12	$4CaO.Al_2O_3$
Gypsum	-	3	$CaSO_4.2H_2O$

The hydration products of C_3S is given as follows:

$$\mathbf{2Ca_3SiO_5 + 7H_2O \rightarrow 3CaO.2SiO_2.4H_2O + 3Ca(OH)_2 + 173.6\ KJ} \qquad (\mathbf{2-1})$$

In short hand terms, generally used for cement hydration products, the above equation can be written as:

$$\mathbf{C_3S + H \rightarrow CSH + CH} \qquad (\mathbf{2-2})$$

Tricalcium silicate reacts with water quickly producing calcium ions, hydroxide ions and heat. Because of hydroxide ions, the pH of mixture increases over 12. This initial reaction decelerates within minutes, which caused decrease in heat evolution. Till the saturation reached, the production of the calcium and hydroxide ions slowly continues. At the

saturation point, calcium hydroxide starts to crystallize. Calcium silicate hydrate also starts to form at the same time. Ions continue to precipitate out of solution which accelerates the conversion of Tricalcium silicate to calcium and hydroxide ions which started the evolution of heat to start again drastically.

The formation of the calcium hydroxide and calcium silicate hydrate provide "seeds" upon which more calcium silicate hydrate can form. As the CSH crystals grow thicker, it becomes more difficult for water molecules to reach C_3S. Therefore, the speed of CSH formation decreases with its coating getting thicker (La Roij et al, 2012). General hydration curve of C_3S is given in **Figure 2-2**.

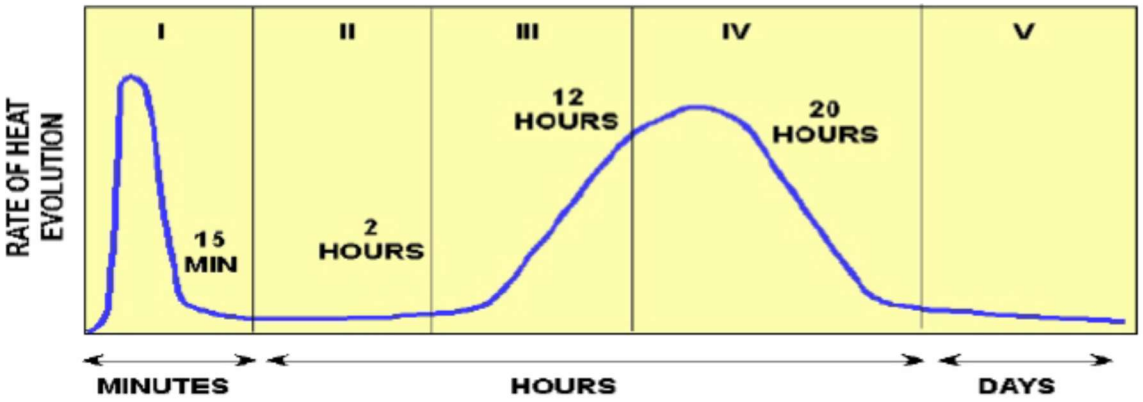

Figure 2-2: Hydration of Portland cement (La Roij et al, 2012)

Based on heat of hydration curve, the hydration reaction of C_3S can generally be divided in 5 stages. The stage I occur in just few minutes during or immediately after mixing, a sharp increase and then decrease in heat of hydration is observed. Stage II is known as the dormancy period in which hydration reaction slows down significantly. It can last for few hours and it is modified by use of retarders to achiever required thickening time for

cement slurries. Until stage II, very less amount of C_3S is hydrated, which starts to hydrate very quickly in stages III and IV. Thus, the cement slurries start to harden and the heat evolution increases. By stage V, cement is set, hardened and less porous, which inhibits the flow of ions and water for hydration. Hence, hydration rate is reduced significantly, hydration continues at slower rate and cement microstructure gets denser (Michaux et al 1990 and La Roij et al, 2012).

Dicalcium silicate also affects the strength of cement by reaction with water, but as its reaction is slower, so the effect is observed in final strength. In addition, the released heat is much lower than that observed in the hydration of C_3S. Nevertheless, the products from the hydration of C_2S are the same as those for C_3S as shown in Equations 2-3 and 2-4:

$$\mathbf{2Ca_2SiO_4 + 5H_2O \rightarrow 3CaO.2SiO_2.4H_2O + Ca(OH)_2 + 58.6\ KJ} \qquad (\mathbf{2-3})$$

In simpler terms:

$$\mathbf{C_2S + H \rightarrow CSH + CH} \qquad (\mathbf{2-4})$$

C_3A concentration is very low in cement, but its reactivity is higher than C_3S. It can affect rheology and early strength development. Unlike CSH, Calcium aluminate hydrate (CAH) formed because of C_3A hydration is not amorphous and it does not form protective layer. Gypsum is added to control the C_3A hydration; else, C_3A hydration can result in premature stiffening of cement, called as Flash set. Tetra calcium aluminate ferrite (C_4AF) hydration is like C_3A, but is much slower (Michaux et al, 1990).

Generally, the cement hydration is described with C_3S hydration, as it is the major constituent of cement. However, hydration of cement is generally complex as hydration of each compound happens simultaneously at different rates. Thus, one compound may influence the reaction of another compound. In addition, the hydration reaction explained above is at ambient temperature. Increase in temperature increases the hydration rate of cement initially but the degree of hydration and ultimate strength remains lower (Michaux et al, 1990).

Studies shows that CSH gel is a good binder up to 230°F, above this temperature CSH gel convert into crystalline α-C2SH, which has higher density than CSH. This results in shrinkage, which affects integrity of cement, and increase in permeability of set cement and decline in the compressive strength. This phenomenon is called strength retrogression. To avoid strength retrogression, reducing C/S ratio from 2 to 1 is proved to be successful, which is achieved by the addition of a silica source, generally silica flour or silica sand. Generally, 35-40% of silica flour or silica sand is sufficient to counter strength retrogression (Nelson, 1990).

Iverson et al. 2010 showed that as the temperature reached 550°F, 40% silica flour was not enough for the strength retrogression. Similarly, as the temperature was increased further, silica quantity of 60-80% might be needed. The addition of crystalline silica in the form of silica flour to the cement mix at temperature range of 230°F to 300-350°F, results in the transformation of C-S-H to Tobermorite which results in low permeability and higher compressive strength of the cement (Iverson et al., 2014). At temperatures

above 350°F, the reaction of silica with cement and water gives Xonotlite instead of Tobermorite. Xonotlite results in significantly smaller increase in permeability while the compressive strength is increased (Joel and Iseghohi, 2009).

Thomas et al. 2009 proposed the nucleation seed theory, which explains the reaction of silica products in cement hydration. According to this theory, silica-containing materials reacts with calcium ions released by hydration of cement to form C-S-H, which then seeds the hydration process further. Pang et al. 2014 evaluated Nanosilica as accelerator for OWC at lower temperatures. In the study, nucleation-seeding theory was further confirmed. Nanosilica worked as a nucleation site for CSH, which stimulates CSH growth that in turn results in uniform microstructure with less porosity and enhances the set cement properties. It was noticed that effect of Nanosilica was much significant in low-density slurries, because of more pore spaces available for CSH growth (Pang et al, 2014).

2.7 CEMENT SLURRY DESIGN PROCESS

The behavior of OWC slurries must be optimized to achieve effective well cementing operation. The appropriate cement slurry design for well cementing is selected by considerations, described in API RP 65-2, such as:

- Laboratory tested slurry design
- Pore pressure/fracture gradient window
- Use of spacers/pre-flushes

- Proper density
- Proper rheological hierarchy
- Fluid compatibility

Sauer and Laundram (1985) presented a step-by-step approach to design cementing jobs in a cost-effective manner. Case histories for three different geological locations were also included where the systematic approach was applied successfully with significant cost saving. Sauer (1987) presented a comprehensive review of the past and present work on mud displacement during cementing. All the topics related to cementing jobs such as centralization, pipe movement, pipe-lowering speed, hole geometry, job monitoring and the application of each process to the mud displacement process is discussed.

Collection of data and its analysis is the first step for designing any cementing job. Quality of information available is the key for any successful cementing job. The data that is analyzed can be divided generally in three categories (Rae, 1990):

- Depth/Configurational data
- Wellbore environment
- Temperature data

Measured and total vertical depth is critically important as depth data affect temperatures, hydrostatic and friction pressures. If the well is deviated, changes must be considered in cement design for efficient mud displacement. Actual hole size through calipers log is

also analyzed as it is necessary for accurate calculation of slurry volumes. Wrong estimation of slurry volumes might result in excessive cost or well security issues.

Type of wellbores to be cemented is analyzed for the presence of formations, like loss circulation zones, over pressured formations, pay zones, salt formations or gas flowing zones. Estimate of pore pressure and fracture pressure is very critical in cement design because wrong values can result in well security issues or fracture of formations. Cement design for pay zones is carefully done to reduce the damage, provide the effective zonal isolation and minimize the risk of gas migration in case of gas. Drilling fluid, which is currently in the well, is also scrutinized and considered for effective displacement by designed cement slurry. Compatibility of mud with cement and spacer is also checked.

Temperature data of the wellbore is also significant in cement slurry design. Bottom hole circulating temperature (BHCT) is used for thickening time estimation. Bottom hole static temperature (BHST) is important for compressive strength development and long-term assessment of cement sheath integrity. Temperature difference between bottom and top of the cement column is also required and cement strength is estimated at top of cement column.

Based on well information available, cement and additives are then selected to design cement slurry matching the specific well objectives and required properties. Density is carefully selected to honor the pore pressure and fracture pressure window, and early strength requirement. Temperature is significant in terms of inclusion of anti-strength retrogression agents in slurry or in case of low temperature wells. Usually a minimum

compressive strength is also required depending on the application as described in **Table 2-5**. This must be considered that regulatory bodies may have different requirements for minimum compressive strength.

Table 2-5: Minimum compressive strength requirement (Cementing Engineering Manual, Dowell, SLB)

Application	Minimum Compressive strength (Psi)
Support casing	500
Early drill out	500
Perforating	2000
Whipstock plug	5000

Fluid loss additives are added based on job type and formation encountered. Recommended fluid loss for different job type is summarized in **Table 2-6**.

Fluid loss additives sometimes may act as viscosifiers so dispersants are then added to improve rheology. Addition of dispersant is required in some cases for efficient mud displacement. While adding dispersants other properties of cement should also be considered as dispersants may act as slight retarder and high dosage may result in development of free fluid and cause sedimentation. Selection of retarder is dependent on the BHCT, type of cement used and slurry composition that helps in modifying thickening time as per the job requirement.

Table 2-6: Recommended fluid loss requirements (Al-Yami, 2015)

Operation	Fluid loss, ml/30 minutes
Prevention of gas channeling	30-50
Liner cementing	< 50
Casing cementing	200 < 300
Horizontal well cementing	< 50
For Squeeze cementing; formation permeability less than 1 md	200
For Squeeze cementing; formation permeability between 1 md and 100 md	100-200
For Squeeze cementing; formation permeability greater than 100 md	35-100
High density slurries	< 50

Cement design is usually an iterative process, initially proposed slurry is then tested in lab and performance evaluated. Based on laboratory tests, the slurry is further improved to suit the specific job (Rae, 1990). A systematic approach was devised by Roshan and Asef (2010) for development of novel cement slurry; defining technical objectives,

recognizing undesired properties at each step and understanding the physicochemical properties of the used additives.

2.8 HPHT WELL CEMENTING

Shaheen et al. (1999) contributed with the specific methodology to design and execute successful cementing job in HPHT wells. It was summarized that accurate well data, BHT prediction and optimized fluids are the key for success. Various tools were also presented which will help in optimizing the cementing design. Criteria for testing cements and spacers at HPHT were also provided.

Shadravan and Amani (2012) reviewed common challenges in drilling HPHT wells. Some of the challenges in cementing HPHT wells are narrow pore pressure/fracture pressure margin, gas migration, strength retrogression, cement shrinkage and effective displacement of mud.

2.8.1 Mechanical Properties of Cement

Heinold et al. (2002) attempted to improve tensile strength of cement mixes. Additives like silica fume, latex, Wollastonite, Polyvinyl Alcohol (PVA), Hydroxyethyl cellulose (HEC), Metakaolin, Sodium metasilicate (SMS) etc. were studied at two different temperatures. HEC, Wollastonite, PVA and SMS exhibited improve in tensile strength at both temperatures. Silica fume and latex increased tensile strength, at one temperature but decreased at other, which indicates the effect of temperature at additive performance. It

was also observed that optimum concentration must be considered for all additives, as beyond optimum value, additives reduce the strength values.

Labibzadeh et al. (2010) evaluated the strength of API class G cement at various temperature and pressure conditions. It was observed that strength increased, as well as it was reaching earlier with increase in pressure and temperature. But, above 121°C, reduction in strength of cement was noticed after reaching the maximum value.

Labibzadeh et al. (2010) evaluated the tensile strength of API class G cement at various temperature and pressure conditions. It was observed that tensile strength increased with increase in pressure and temperature. But above temperature of 150°F, reduction in tensile strength of cement was noticed, the metamorphosis of C-S-H gel to α-C_2SH was suggested as the reason in this study.

2.8.2 Silica as Anti Strength Retrogression Agent

Eilers and Root (1976) studied the long-term effect of high temperature on strength retrogression. It was concluded that 30-40% of silica must be added to stabilize the cement to avoid retrogression, which is caused by production of alpha dicalcium silicate hydrate.

Hodne et al. (2001) conducted an experimental study to analyze the effect of temperature, micro silica and other additives on the cement slurry. Slurry consistency, rheological properties and zeta potential were studied at various temperatures. In general, micro silica increased the rheological properties and decreased the thickening time.

Jupe et al. (2008) studied hydration of API Class H cement at 180°C and higher pressure with different silica sources. Silica flour and zeolite both at 35% addition produced Tobermorite as hydration product. Silica fume delayed the formation of tobermorite, which can be attributed to amorphous form of silica fume, so physical characteristic is also important when using silica as an additive.

Ogbonaa and Iseghohi (2009) presented use of locally available silica for successful HPHT cementing in Nigeria. Locally available silica sand resulted in comparable strength, fluid loss, thickening time and rheological properties as compared to imported silica.

Iverson et al. (2010) studied strength retrogression at higher temperatures in range of 500-650°F with silica flour concentration of 40-80%. It was concluded that, 35% silica flour in high temperature wells could be very low. Xonotlite was the major phase formed in all mixes as confirmed by the Rietveld refinement results. In addition, 30 days curing was considered low for studying strength retrogression as even at 30 days unreacted silica was present in the mix, which was being slowly consumed over the time.

Gibson (2011) documented the use of liquid silica to avoid strength retrogression at higher temperatures. It was revealed that liquid silica was as effective as silica flour in terms of compressive strength, fluid loss and rheology. Liquid silica reduced the health and environment risk, the complexities involved in handling and transporting dry silica and costs involved.

2.9 APPLICATION OF ZEOLITE IN CEMENT

Poon et al. (1999) studied the hydration rate of natural zeolite blended cement pastes. It was concluded that zeolite is a pozzolanic material with reactivity in between silica fume and fly ash. Zeolite replacement reduced the porosity but at high replacement around 25% it increased the porosity. Moreover, it was observed that porosity of the sample had decreasing trend with the curing age, which can be attributed to the increase in pozzolanic reaction with time. Good correlation was seen between porosity and the compressive strength development.

Geztlaf et al. (2004) presented zeolite can be used for various functions. Zeolite improved the strength development by pozzolanic reaction at lower temperatures too. For lightweight slurries, zeolite performance was comparable to conventional silica fume slurries. Zeolite can be used as anti-settling agent for lightweight slurries. Fluid loss was reduced with zeolite addition.

Luke et al. (2004) demonstrated that zeolite could be an effective foam-cement stability agent. It has also been established that zeolite in cement slurries act as good settling agent. It has better fluid loss control and can act as good friction reducer. It was concluded that zeolites having lower mean particle size showed improved rate of early compressive strength.

Fyten et al. (2005) reported the effectiveness of zeolite in economically reducing the ECD while keeping the strength values adequate and no free fluid development. Zeolite

slurry was observed to be thermally stable and having good bonding abilities with the casing and formation.

Cannon (2013) proposed zeolite should be studied for HPHT well applications. Initial results revealed increase in compressive strength and decrease in free water with replacement of cement with zeolite. It was observed that as the particle size of zeolite decreased, the compressive strength increased but rheology was also affected negatively.

Sedic et al. (2015) presented the use of zeolite as an admixture for Carbon dioxide injection well. With its pozzolanic nature, zeolite may react with all the $Ca(OH)_2$ in the cement to further form secondary hydration products, hence reducing the susceptibility of cement to CO_2 attack.

2.10 NANO MATERIALS STUDIED IN CEMENT

Ershadi et al. (2011) proposed Nanosilica as an additive for reduction in permeability and porosity of hardened cement with increase in compressive strength. Nanosilica not only increased the ultimate strength, but also improved the early strength significantly. It was also observed that Nanosilica reduced thickening time significantly, reduced the fluid loss and increased plastic viscosity and yield point.

La Roij et al. (2012) used patented active nanotechnology, which comprised of minerals like alkali metals, zeolites, alkali metals silicates and calcium carbonate etc. with API class G cement. Employed active Nanotechnology increased compressive strength,

elasticity and chemical resistance owing to the dense crystalline fiber like structure after hydration that blocks capillary pores.

Santra et al (2012) studied the effect of nanomaterials on OWC hydration and mechanical strength. Multiwalled nanotubes used in the study did not enhance the mechanical properties. Compressive strength development is directly related to the extent of hydration that is studied in this research with isothermal calorimetry. It was confirmed that cumulative heat of hydration plot could be a good tool to predict the compressive strength development of cement especially at early stages.

Patil and Deshpande (2012) used Nanosilica with latex in Oil-well cement. Nanosilica exhibited increase in both early and final strength with a slight decrease in the fluid loss. Effect of temperature on performance of Nanosilica showed it could be used at various temperatures.

Pang et al. (2014) showed the application of Nanosilica as an accelerator for low temperature wells (59°F) with API class H cement. Cement hydration kinetics with different types of Nanosilica was studied at normal density i.e. 16.6 ppg and lower density i.e. 13 ppg. At 16.6 ppg, cumulative heat evolution of Nanosilica slurry was comparable to currently used accelerator ($CaCl_2$). However, the enhancement of hydration and thus strength in 13 ppg slurry was very significant as compared to $CaCl_2$. It was also established that Nanosilica with smaller particle size and higher aspect ratio tend to increase the hydration.

De Paula et al. (2014) employed carbon nanotube grown directly on cement clinkers for Oil-well cements. Compressive strength was reported to be unaffected while increase in tensile strength was observed with small quantity of carbon nanotube.

Rahman and Murtaza (2015) considered Nanoclay with class G cement along with other additives for HPHT environment. Nanoclay improved ultimate compressive strength of cement mixture. In addition, it increased the early hydration of cement to gain quicker early compressive strength, which can reduce drilling cost by decreasing WOC time. Moreover, Nanoclay increased the plastic viscosity and acted as retarder by increasing thickening time.

Murtaza et al. (2016) studied microstructural properties along with mechanical properties for cement mixtures containing Nanoclay. Nanoclay improved the compressive strength notably with 1% addition, but further increase in Nanoclay resulted in decrease of strength. Similar trend was observed for permeability. It was confirmed by SEM analysis that dense CSH gel was formed with Nanoclay addition that reduced permeability and improved compressive strength.

Khan et al. (2016) utilized Carbon nanotube with Class G cement mixture containing various other additives at HPHT. Carbon nanotube increased final compressive strength as well as early strength of 2000 psi was achieved in significantly less time than control mixture.

Sun et al. (2016) used combination of cellulose nanofibers (CNF) and graphene nanoplatelets (GNP) with Oil-well cement. Class H cements was used for the study, which determined combination of CNFs, and GNPs resulted in increase in flexural strength and compressive strength. Improvement of flexural strength was much substantial as compared to compressive strength. Increase in strength was attributed to the increased degree of hydration achieved with nanomaterials.

Deshpande and Patil (2017) used halloysite nanotubes and submicron alumina with Oil-well cement. Submicron alumina was used at low temperature of up to 40°F and it accelerated the rate of strength development. Halloysite tubes increased the tensile strength of cement. It was demonstrated that effective dispersion of nanomaterials is necessary to maximize the benefit. Using sonication in presence of dispersant gave the maximum increase of 141%.

CHAPTER 3

EXPERIMENTAL PROGRAM

Cement lab testing is one of the major factors in successful design of cement slurry. Cement prior to placement in well is evaluated for properties like density, rheology, thickening time, compressive strength etc. under the simulated downhole environment. Slurry is then modified and optimized for the well objectives and requirements.

The planned experimental program for this study is implemented per the recommended practice for testing well cements (API Specifications 10B-2) unless specified otherwise. API Specifications 10B-2 outlines the recommended practices for slurry preparation, conditioning and testing various properties of Oil-well cement. Following API specifications make sure that the results obtained are reproducible in the tested conditions. API gives general recommendation for testing cement that should be followed as close as possible, but different country laws and some well conditions might be considered while testing slurries. API recommends documenting any change from the API specifications while performing experiment.

The properties of cement included in this research are:

a. Thickening time
b. Density
c. Rheology

d. Free water separation

e. Static fluid loss

f. Compressive strength test

- Compressive strength by crushing method
- Compressive strength development by sonic method

g. Tensile strength

h. Porosity and permeability

i. Microstructural analysis

- XRD
- SEM

3.1 WELL SPECIFICATIONS

A cement design of typical well in Saudi Arabia has been selected to test the behavior of Nano Zeolite on cement design performance. The specifications of selected well are presented in **Table 3-1**, temperature and pressure conditions at which slurry properties are assessed were based on the selected well specifications.

Based on selected well specifications and API specifications, temperature and pressure conditions to evaluate different cement properties are selected as shown in **Table 3-2**. Rheology and free fluid was evaluated at standard temperature of 190°F. Static fluid loss was performed at 190°F and standard pressure of 1000 psi. Thickening time temperature was selected to be 228°F based on BHCT of the well. Pressure was calculated by adding

hydrostatic pressure exerted by mud column to surface pump pressure. For compressive strength and tensile strength, temperature was raised to BHCT 228°F in 49 minutes (time to reach bottom) and then increased to 290°F in 191 minutes with pressure of 3000 psi.

Table 3-1 : Typical well specifications

Well Parameters	Values
Depth of well (TVD)	14000 ft.
Bottom Hole Circulating Temperature (BHCT)	228°F
Bottom Hole Static Temperature (BHST)	290°F
Time to reach bottom	49 min
Mud Weight (MW)	11.4 ppg
Bottom Hole Pressure (BHP)	8300 psi
Surface pump pressure	1050 psi

3.2 MATERIALS

Cement slurries used in this study are prepared using high sulfate-resistant API Class G Oil-well cement with a specific gravity of 3.14. Further chemical properties of Class G cement used is summarized in **Table 3-3**. All the cement slurries have been prepared using tap water. Several conventional chemical admixtures provided by Halliburton have been used as shown in **Figure 3-1**.

Table 3-2: Pressure and temperature conditions for several tests

Properties	Temperature	Pressure
Rheology	190°F	Atmospheric
Free water content	190°F	Atmospheric
Fluid loss	190°F	1000 psi
Thickening time	228°F	9400 psi
Compressive strength	290°F	3000 psi
Tensile strength	290°F	3000 psi

Table 3-3 : Chemical composition of Class G cement

Chemical Component	Weight (%)
Silica (SiO_2)	16.33
Alumina (Al_2O_3)	2.75
Iron Oxide (Fe_2O_3)	5.98
Calcium Oxide, Total (TCaO)	68.63
Magnesium Oxide (MgO)	1.75
Sulphur Trioxide (SO_3)	3.09

Figure 3-1: Additives used in experiments

The functions and concentrations of all the additives used in research are explained in **Table 3-4**.

Table 3-4 : Commercialized additives with their functions and percentages

Additives	Functions	Concentration (%BWOC)
SSA-1	Strength stabilizing agent	35
MBHT	Expanding agent	1
HR-12	Retarder	0.7
CFR-3	Dispersant	1
Halad-344	Fluid loss controlling agent	0.2
Halad-413	Fluid loss controlling agent	0.5
DA-3000	Anti-foaming agent	0.25/10bbl

3.3 PROPERTIES OF NANO ZEOLITE

Because of the increase in surface to volume ratio, nanoparticles have the maximum number of exposed surface atoms---which results in much improved chemical properties than micro particles. The nano-scale behavior of many materials has been explored in the last few years, but application of Nano zeolites is just in its early age. This can be attributed to the fact that synthesis of Nano zeolite is expensive and not yet suitable for industrial application. (Severance, 2014)

Current challenge for use of Nano zeolite lies in its synthesis but recent progress implies the efficient preparation of Nano zeolite designed for different applications is not far away. Research is currently being done to optimize their synthesis, which will be cost effective and can be used for industrial production of Nano zeolite. (Mintova et al., 2013). As more than 40 types of Zeolites are available naturally, zeolite nanoparticles can be obtained by milling.

Planetary ball milling was used by Charkhi et al in 2010 to get particle size as small as 100nm, but large particle size distribution was the problem and loss of crystallinity was also observed. Kong & Tsuru, 2010 prepared zeolite Nano particles from zeolite micro particles without affecting its crystalline structure by mechanical-stress-induced fracture. Different size of Nano zeolite was obtained by varying the centrifugation process and time, eliminating the problem of wide spread particle distribution. Wakihara et al 2011 use bead milling process and then later used recrystallization to repair any distorted

crystal structure during the milling process. Further studies are required to consider these methods for industrial application.

XRF analysis was performed to confirm the chemical composition of Nano zeolite used in this study, which is presented in **Table 3-5**.

Table 3-5: XRF analysis of Nano zeolite

Compound	SiO_2	Al_2O_3	Fe_2O_3	CaO	Total
Concentration	61.30%	30.33%	1.24%	4.27%	97.14%

SEM and TEM analysis of Nano zeolite particles used in this study are shown in **Figure 3-2** and **Figure 3-3**.

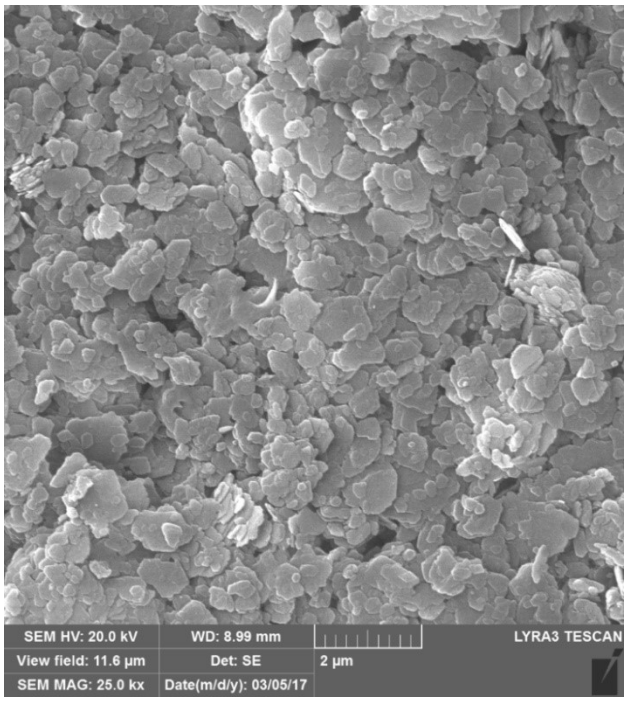

Figure 3-2: SEM image of Nano zeolite at 2µm

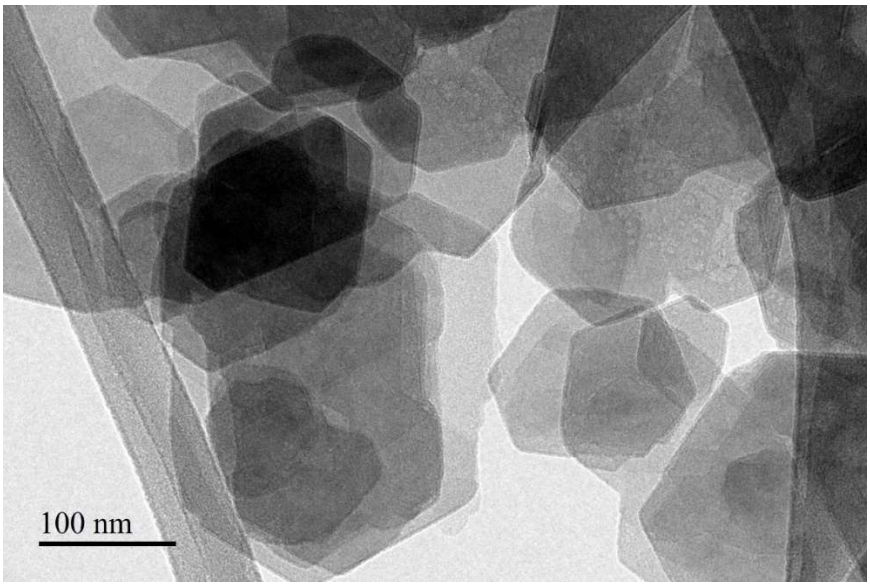

Figure 3-3: TEM image of Nano zeolite with particle size

It can be observed that Nano zeolite particles are less than 1 micrometer that is why the structure is not clear with SEM image. TEM image on the other hand shows hexagonal particles of Nano zeolite in size range less than 100 nm, but because of agglomeration of all particles, the structure is not clear. Both SEM and TEM images showed the agglomeration of Nano zeolite particles. Particle size distribution, as provided by supplier, is given in **Figure 3-4**.

3.4 CEMENT SLURRY PREPARATION

The preparation of cement slurry is critical as the mixing technique can have significant effect on the mixed slurry. The cement slurry is prepared using a variable speed high-shear blender type mixer with bottom drive blades as per the API Specifications (see **Figure 3-5**).

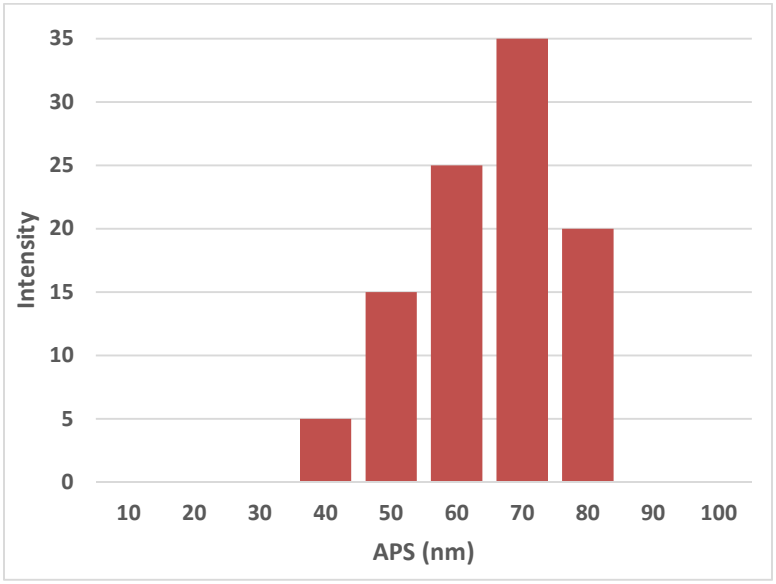

Figure 3-4: Average particle size (APS) of nanozeolite particles used (provided by supplier)

Figure 3-5: High speed blender

For additives mixing in cement, there are two methods specified in API standards. The first method is blending of additives in the cement before mixing with water and is called dry mixing. The second method is wet mixing, which requires additives to be mixed with water before the addition of cement powder. Silica flour is generally dry blended with cement before adding to water. In this experimental study, cement slurry was prepared in accordance with API Recommended Practice 10B-2. Wet mixing is used for all the additives mixing. Silica flour is dry blended with cement. Tap water is used for all mixes.

For slurry preparation, cement and all other additives are weighted according to the cement design to prepare 600ml slurry that will be sufficient for all tests. Defoamer is added in water before other additives. All the additives are then added in water while mixing at 4000RPM, after all the additives mixed in water, cement and silica flour blend is added. Cement was added slowly at uniform rate to avoid any slumps in slurry. All the additives and cement blend is added within 3 minutes. Then slurry was mixed at high speed of 12000 RPM using electric mixing unit for 35 seconds. Nano zeolite is dry blended with cement and silica flour in all cases. After that, slurry was put in atmospheric consistometer, as shown in **Figure 3-6** for consistency measurement for 30 minutes at 190°F and atmospheric pressure.

3.5 THICKENING TIME

The thickening time explains the period within which cement slurry remains pumpable under simulated well conditions (Dwight, 1990). The laboratory test conditions should

represent the time, temperature, and pressure to which cement slurry will be exposed during pumping operations.

Figure 3-6: Atmospheric consistometer

To determine the thickening time, the consistency of cement slurry, expressed in Bearden units of consistency (Bc), is measured using the HPHT consistometer as shown in **Figure 3-7**.

HPHT consistometer incorporates a rotational cylindrical slurry container equipped with a stationary paddle assembly, all sealed off in a pressure vessel capable of enduring well-simulation pressures and temperatures. Consistency of slurry is determined by the force imposed by the slurry against the paddle and measured as a torque. A potentiometer, or

its equivalent, is used to determine the torque. The slurry container is revolved at a speed of 150RPM.

Figure 3-7: HPHT consistometer

First, the cement slurry is prepared according to API Specifications and then it is poured in HPHT consistometer cup and placed in HPHT consistometer. After placement, the test conditions are applied. During the thickening time test, increase the temperature and pressure of the cement slurry in the slurry container in agreement with the applicable well-simulation test program. Then the test is conducted up to the time at which the slurry reaches a consistency considered satisfactory to make it unpumpable (for example 70 Bc or 100 Bc). Consistency value of 100 BC was considered as thickening time in this study.

3.6 DENSITY

Density of cement was evaluated by using pressurized mud balance as shown in **Figure 3-8**. Pressurized mud balance removes any entrapped air and gives accurate density. Cement slurry is prepared according to API specification and conditioned at 190°F and atmospheric pressure. Conditioned slurry was then used for density measurement.

Figure 3-8: Pressurized mud balance

3.7 FREE WATER CONTENTS

The free fluid test helps determine the capacity of the cement slurry to prevent fluid separation in static conditions - both during placement, and after it has been placed into the wellbore. Excessive free fluid in slurry can cause problems with water pockets, channeling, sedimentation, zonal isolation, etc. For the measurement of free fluid contents, the cement slurry was prepared and conditioned as explained earlier. Cement was then poured into graduated cylinder up to the 250ml mark, and was covered with

aluminum foil to prevent evaporation for 2 hours (See **Figure 3-9**). Later, the amount of water on top is measured in milliliters (ml).

Figure 3-9: Free water content test

3.8 RHEOLOGICAL PROPERTIES

The rheology of cement is critical for effective displacement of drilling fluid and calculating the friction pressures. Rheological properties are measured using variable speed rheometer in **Figure 3-10**.

The conditioned slurry is poured into the rheometer cup that was pre-conditioned at 190°F. The slurry is stirred for about 10 seconds at 3 rpm, 6 rpm, 100 rpm, 200 rpm, and

300 rpm. Viscosity readings are recorded at every speed first in ascending order and then descending order.

Figure 3-10: Variable speed FANN rheometer

The following rheological properties are calculated using Bingham plastic model using the average viscosity values at different speed:

- Plastic viscosity
- Yield point

Gel strengths can be measured by newly prepared slurry or the same slurry used for rheology as per API. Slurry used in rheology was used for gel strengths measurement.

Slurry was stirred for 60s at 300rpm to make it homogenous. Then viscometer was stopped for 10 seconds and then started at 3rpm, the maximum value recorded is called initial gel or 10 sec gel. Later, the slurry was kept static for 10 minutes, then rheometer was started at 3 rpm and maximum dial reading obtained is the 10-minute gel.

3.9 COMPRESSIVE STRENGTH

The compressive strength is one of the most important property of cement, which will determine the integrity of cement and ability of cement sheath to hold the induced stresses over the life of well. Two methods are employed to determine the compressive strength of cement. First is the non-destructive sonic determination of the compressive strength of the cement using Ultra Cement Analyzer (UCA). Second is the destructive method of Unconfined Compressive Strength (UCS) by applying load to square inch cement cubes.

3.9.1 Compressive Strength by Sonic Method

The sonic strength test by UCA is a non-destructive test performed on cement slurry to estimate its strength. Correlations have been developed to approximate the compressive strength of a cementing composition based on the time required for the ultrasonic signal to pass through the cement as it sets. UCA gives the compressive strength development of the slurry over the time. Sonic strength is observed to underestimate compressive strength to some extent, but due to the advantage of compressive strength development over time it is widely used for field operations.

The compressive strength of cement slurry is measured by placing slurry in UCA (shown in **Figure 3-11**) with temperature and pressure adjusted to simulate downhole conditions. An acoustic signal is then transmitted through the cement sample. As the strength of the cement increased over time, the acoustic signal travels through the sample with higher speed, reducing the transit time that is then used to calculate the compressive strength.

Figure 3-11: Ultrasonic cement analyzer (UCA)

First, the cement slurry is prepared and conditioned in atmospheric consistometer as described in section 3.4. At the end of conditioning, the cement slurry is poured in the cell of UCA (see **Figure 3-12**).

The cell is placed in the UCA chamber and the test conditions are applied as per the schedule described in **Table 3-2**. Each test is conducted for 24 and 48 hours. At the end of test duration, the system is cooled and cement sample is removed from the cell.

Figure 3-12: UCA cell

3.9.2 Compressive Strength by Crushing Method

The crush strength test indicates the strength of cement slurry after it has been pumped into the well and allowed to set static. The slurry is subjected to temperature and pressure for various lengths of time as per the well conditions and requirements. Cement cubes are cured using molds in Curing Autoclave (see **Figure 3-13**).

After demolding, cured cubes are crushed in uniaxial crushing equipment to measure maximum load cement can bear before crushing which is then used to compute compressive strength.

Figure 3-13: Curing autoclave

In this test, first the cement slurry is prepared and filled in the chambers of the prepared molds (**Figure 3-14**), covered with the top plate, and immediately placed in a curing autoclave.

Temperature and pressure condition is applied in accordance with the test schedule given in **Table 3-2**. At the end of test duration, the molds with set cement are removed and cubes are detached from molds (see **Figure 3-15**).

Figure 3-14: Cement moulds

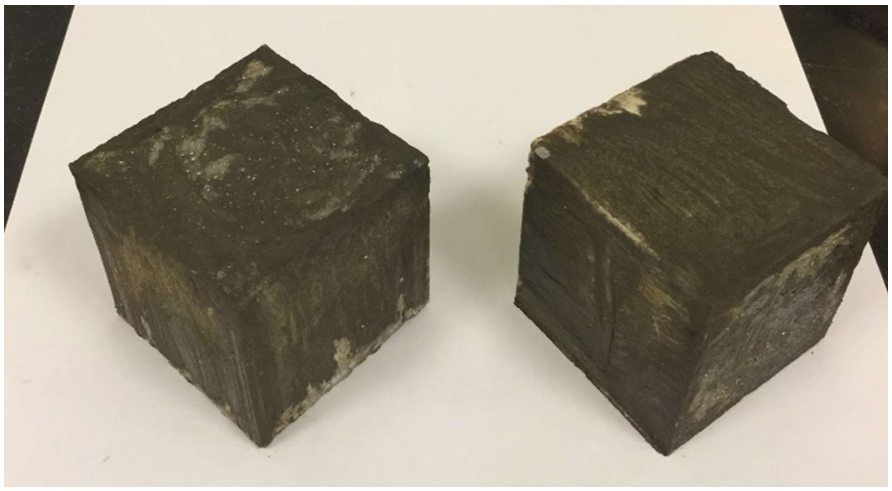

Figure 3-15: Cubes of cement (2×2) sq. inches

Later, the cubes are crushed in universal testing equipment to get compressive strength results (see **Figure 3-16**).

Figure 3-16: Crushing of cubes in universal testing equipment

3.10 TENSILE STRENGTH

If there are enough induced stresses to cause mechanical failure, tensile failure is more likely to happen than compressive. Thus, evaluation of tensile strength is critical for engineers to assess the failure criteria for set cements (Heinold et al, 2003). Currently, there is no standardized way of testing Oil-well cement by API for tensile strength. Researchers are using direct tensile test method and indirect split tensile strength as specified in ASTM for concrete mix, which might give different values for same mix (Heinold et al, 2003).

For tensile strength, indirect method of Splitting Tensile Strength (STS) is used in current research as described in ASTM Standard C496. Cylinders of dimension 3in length and

1.5in diameter (L/D ratio = 2) were molded and cured for 24 hours by same pressure and temperature schedule described for crushing strength. After removing the cylinders from molds, small wooden strips of thickness 1/8in and width 1in were placed on the top and bottom of cylinder so that load is distributed uniformly. Cylinders are placed in horizontal direction and then crushed as shown in **Figure 3-17**. Examples of good failure and bad failure after tensile strength test are shown in **Figure 3-18**.

Figure 3-17: Cylindrical sample for split tensile strength after crushing

Splitting tensile strength is then calculated as given below:

$$\text{STS} = \frac{2 * \text{Max load at break}}{\pi * \text{Length} * \text{Diameter}}$$

STS results of cylinders vary with the sample size even if the aspect ratio is kept constant, as reported by Heinold et al 2003. Also, the results of direct uniaxial tensile strength test (UTS) will also be different than splitting tensile strength test. To account

for the size effect and different type of tests, Heinold et al 2003 presented a correlation to convert STS data to UTS data:

$$\text{UTS} = \text{STS} * (0.025 * Volume_{cylinder} + C_{combined})$$

Where,

UTS = Uniaxial tensile strength (direct)

STS = Splitting tensile strength (indirect)

$C_{combined}$ = 0.43, constant

Figure 3-18: Bad failure (left) and good failure (right) (James and Boukhelifa, 2008)

3.11 STATIC FLUID LOSS

Static fluid loss test is performed to estimate the amount of fluid loss under a differential pressure when slurry encounters permeable formation. Stirring and non-stirring fluid loss

equipment can be used for fluid loss measurement at desired temperature and pressure conditions. Usually when the temperature is above 190°F, stirring fluid loss equipment is used, as slurry can be conditioned in the stirring fluid loss cell at required temperature.

Non-stirring fluid loss equipment is used in this study as shown in **Figure 3-19**. Static fluid loss test was performed at 190°F and 1000 psi pressure as per API standards. Cement slurry is prepared and conditioned as explained earlier before subjecting it to test conditions for 30 minutes. At the end of test, the amount of collected fluid loss is measured using graduated cylinder.

Figure 3-19: Non-stirring static fluid loss equipment

If the test duration of 30 minute is completed, API fluid loss, expressed in ml/30min, is calculated by:

$$\text{API fluid loss} = 2 \times V_{30}$$

Where,

V_{30} = Volume of filtrate collected at 30 minutes, in milliliters.

For tests that blow dry in less than 30 minutes, calculated API fluid loss is given by:

$$\text{Calculated API fluid loss} = 2V_t * \sqrt{\frac{30}{t}}$$

Where,

V_t = Volume of filtrate collected at the time Nitrogen blows through, in milliliters.

t = Elapsed time, in minutes.

3.12 PERMEABILITY & POROSITY TESTS

Permeability determines the ability of fluid to flow through set cement and it is one of the critical properties in determining long-term integrity of cement. The cement sheath is supposed to have lower permeability to seal the zones and prevents fluid migration under HPHT conditions. Porosity determines the void spaces in the set cement, which can store any foreign fluid that can be detrimental for the cement sheath.

Plug samples were drilled out from untested cubes of cement. The samples were then end faced grinded to get clean parallel surface. Core samples, as can be seen in **Figure 3-20**,

were dried under vacuum for about one day. Average length and diameter of core plugs were determined from four different points along the length and diameter. The dry weights of core plugs were recorded. Porosity and permeability were measured under confining pressure 500 psi with Automatic Porosimeter/Permeameter shown in **Figure 3-21**.

Figure 3-20: Core samples for porosity and permeability

Figure 3-21: Automatic Porosimeter/Permeameter

3.13 MICROSTRUCTURAL ANALYSIS

The microstructure of cement slurry is studied using both SEM and XRD analysis. SEM explains the composition, topography and pore structure and XRD is a well-known technique for studying cement composition and hydration. A scanning electron microscope (SEM) scans the sample and images with the beam of electrons. It explains the composition and structure of a sample. X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material. Using XRD spectra, several compounds in hydrated cement paste such as calcium hydroxide (CH, portlandite), calcium silicate hydrate (C-S-H), tobermorite etc. can be detected. For the XRD analysis, the cement samples are crushed to powder form and in SEM analysis, the small pieces of cement samples are used.

CHAPTER 4

EXPERIMENTAL INVESTIGATIONS OF NANO ZEOLITE WITH CLASS G CEMENT

This chapter describes the results of study on the effect of Nano zeolite on neat class G cement properties. The results of laboratory tests at various concentrations of Nano zeolite are discussed here along with the class G results for comparison.

4.1 CEMENT SLURRY DESIGN

Normal density slurry of 15.8 lb/gal was used with recommended water/cement ratio of 0.44 for class G as specified in API Spec 10A. The effect of Nano zeolite on various cement properties was examined at varying dosages of 0-3%. The slurry composition for all the mix designs used in this part of study can be seen in **Table 4-1**.

Mix design labelled as 'G' will serve as the control mix for comparison. Nano zeolite was then incorporated in the cement slurry in different percentages i.e. 1%, 2% & 3% by weight of cement (BWOC) and are labelled as 'G1', 'G2' and 'G3' respectively.

Table 4-1 : Mix design of cement slurries with different concentration of Nano zeolite

Component	Mass (percentage by weight of cement)			
Class-G cement	100	100	100	100
Water	44	44	44	44
Nano zeolite	0	1	2	3
Mix design label	G	G1	G2	G3

4.2 EFFECT OF NANO ZEOLITE ON FREE WATER CONTENT

Free water is water that might be separated from the cement slurry and accumulated at top of cement, which can result in particles settling effect. Results are tabulated in **Table 4-2**. Results indicate that Nano zeolite did not cause any free water separation.

Table 4-2: Variation of free water contents of cement slurries with Nano zeolite

Cement Slurries	G	G1	G2
Free water (ml/250ml)	0	0	0

4.3 EFFECT OF NANO ZEOLITE ON RHEOLOGY

The rheological properties of an Oil-well cement (OWC) slurry defines the quality of the final product and assists predicting its end use performance and physical properties during and after pumping. Rheological measurements determine the flow properties of the cement slurry such as plastic viscosity, yield point, gel strength, etc. Variation of class

G cement's rheological properties with the addition of Nano zeolite is presented in **Figure 4-1** and **Figure 4-2**.

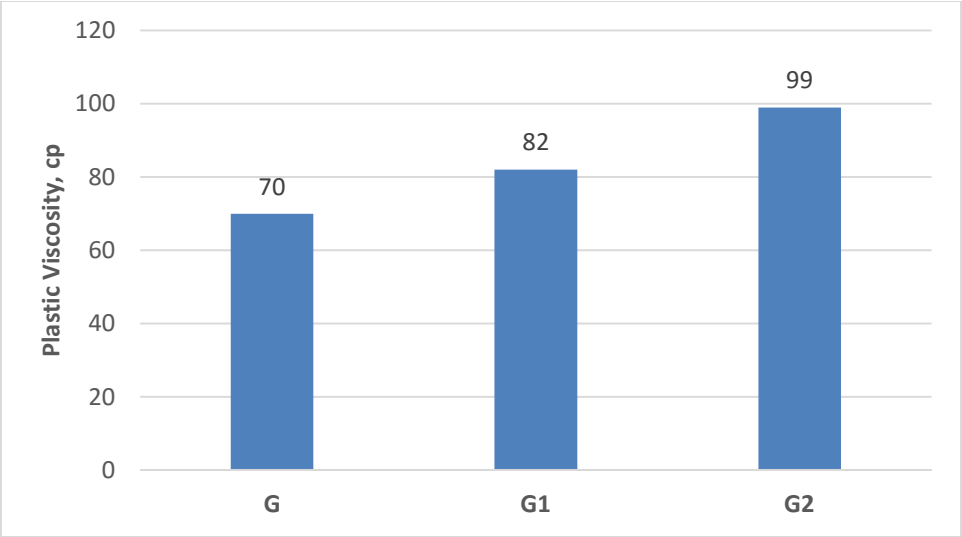

Figure 4-1: Plastic viscosity variation for different concentrations of Nano zeolite

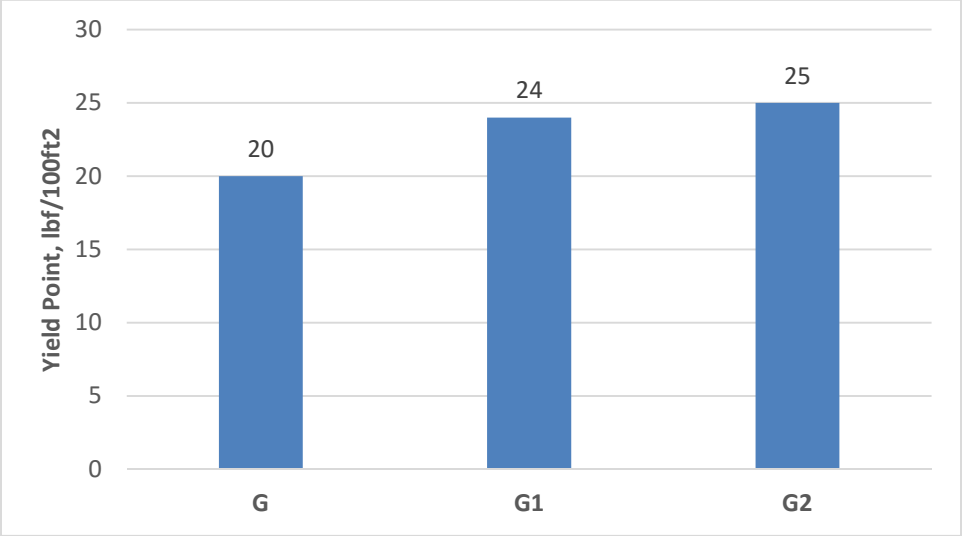

Figure 4-2: Yield point variation for different concentrations of Nano zeolite

Nano zeolite increased the plastic viscosity and yield point of the class G cement. This can be attributed to the smaller particle size of Nano zeolite, which increased the friction between the particles resulting in the increase in plastic viscosity and yield point. It can be observed that increase in viscosity is significant, however, if required, small amount of dispersant can be added to modify the plastic viscosity according to the specific job requirement. Increased yield point indicates the slurry ability to suspend solid particles, while flowing, improves with the addition of Nano zeolite.

Gel strength is the measure of attractive forces in particles that cause the development of gelation when flow is stopped. It also explains the force required to initiate the flow after stopping circulation. Results for gel strength test are summarized in **Figure 4-3**.

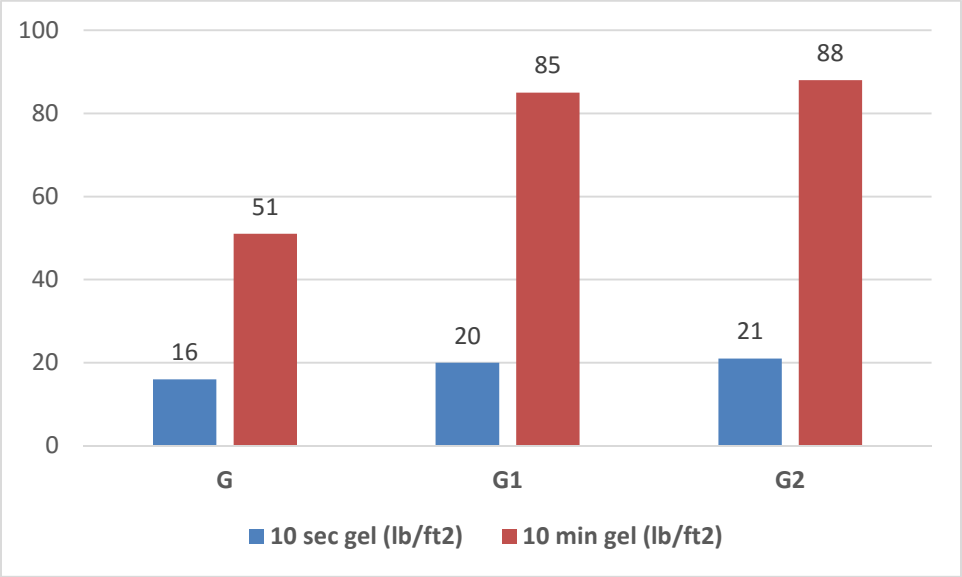

Figure 4-3: Effect of Nano zeolite on gel strength of Class G cement

Nano zeolite tends to increase both the 10-second and 10-minute gel strength. Increase in 10 min gel strength is more significant than 10 sec gel strength. Higher gel strength indicates better particle suspending ability while slurry is in static condition. This means that particles will not settle down if slurry will be static in well for a longer time. Settling of particle may result in altered density, which can cause loss circulation or inflow. But higher gel strength means more pressure will be required to initiate the flow if the slurry remains static for long time. However, this can be overcome by the addition of small amount of dispersant.

4.4 EFFECT OF NANO ZEOLITE ON COMPRESSIVE STRENGTH

The compressive strength measures the integrity and stability of cement to sustain long term imposed stresses. Cement slurry is supposed to develop the compressive strength early and make strong bond with walls of well after the placement. So, the drilling operations can be resumed in short time. Therefore, compressive strength tests are conducted to evaluate the development of cement strength with time utilizing the ultrasonic cement analyzer (UCA).

Neat class G cement with and without Nano zeolite has been subjected to the UCA test conducted under temperature 290°F and pressure 3000 psi for 24 hours. Sample chart of compressive strength development for slurry G2, as provided by the UCA data acquisition software, is shown in **Figure 4-4**. Compressive strength development of various slurries are presented in **Figure 4-5**, **Figure 4-6**, **Figure 4-7** and **Figure 4-8**.

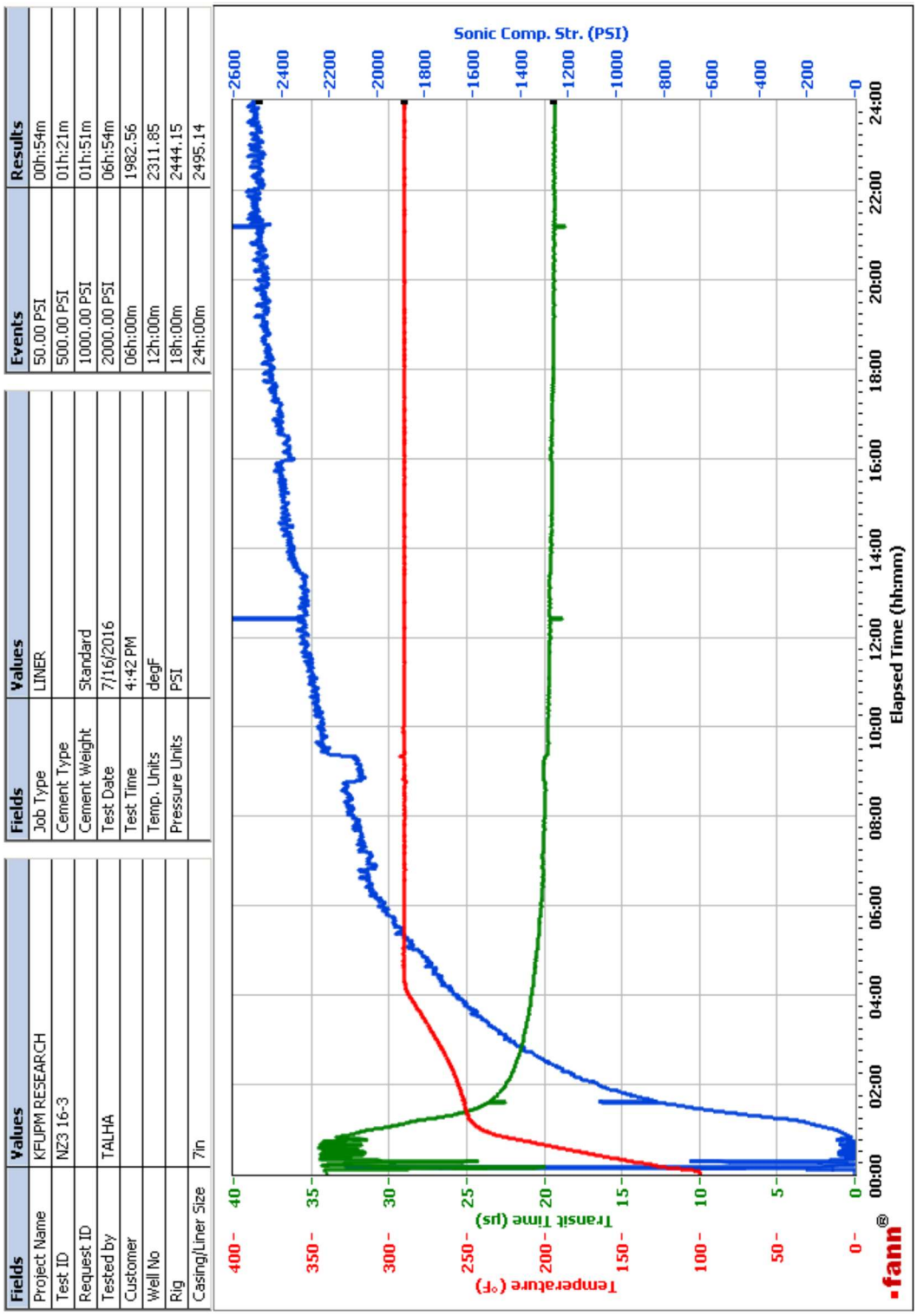

Figure 4-4: UCA sample chart as produced from UCA software for G2 slurry

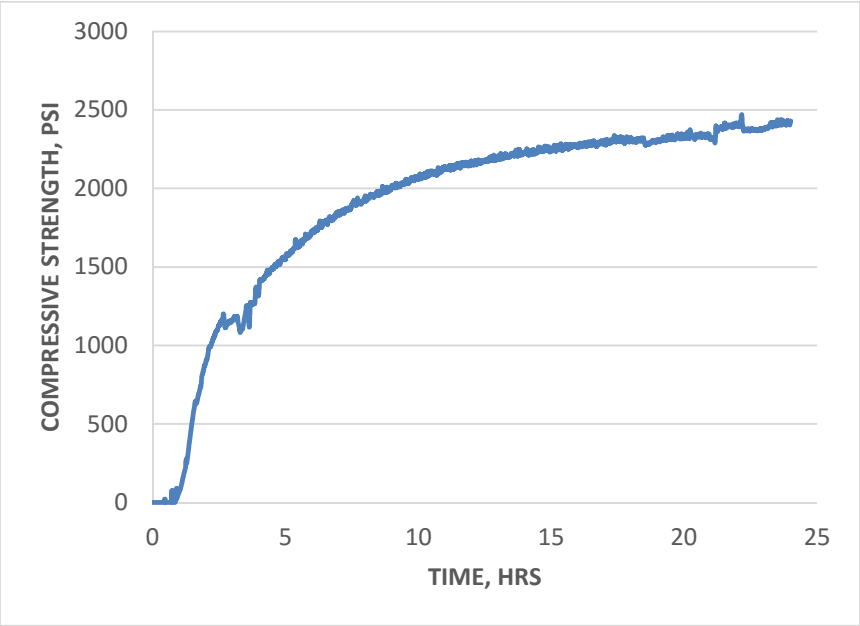

Figure 4-5: Compressive strength development of G slurry

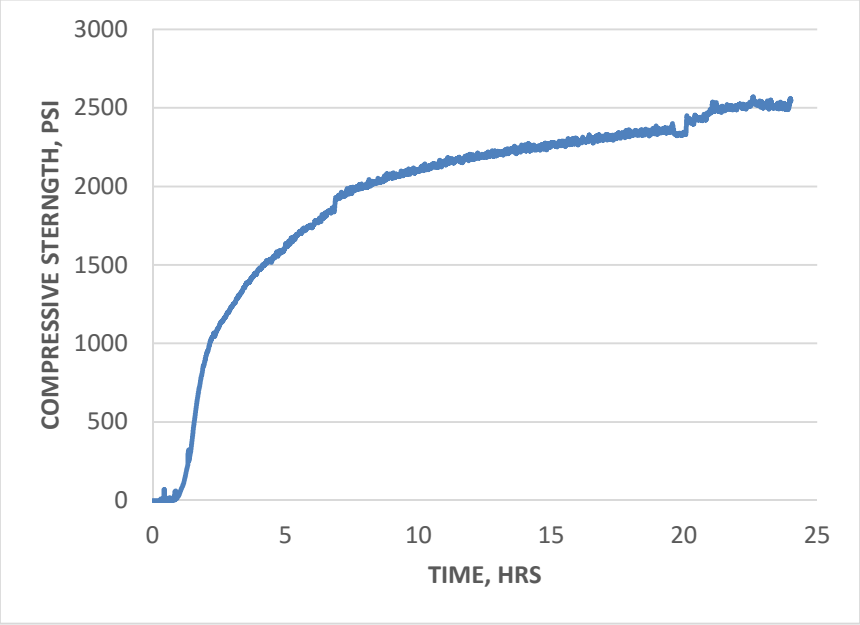

Figure 4-6: Compressive strength development of G1 slurry

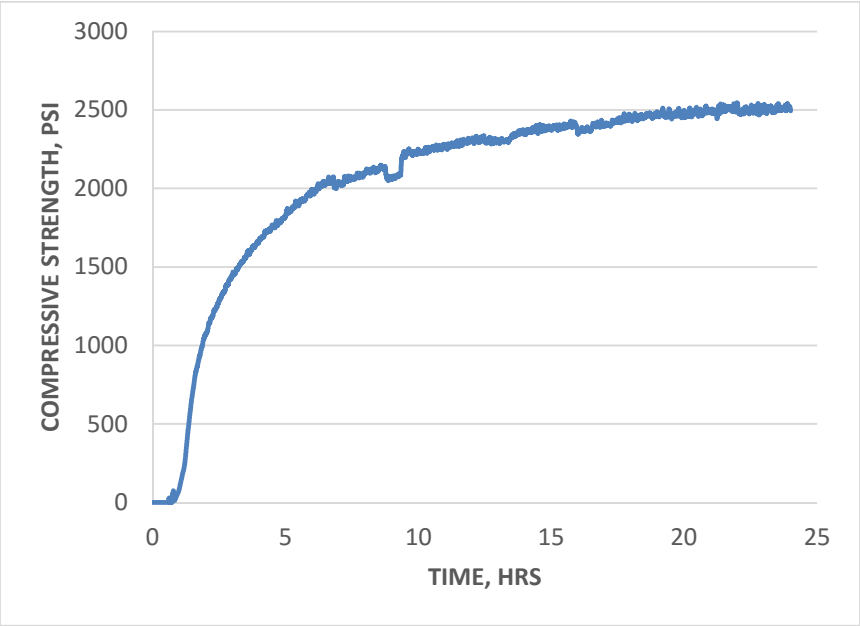

Figure 4-7: Compressive strength development of G2 slurry

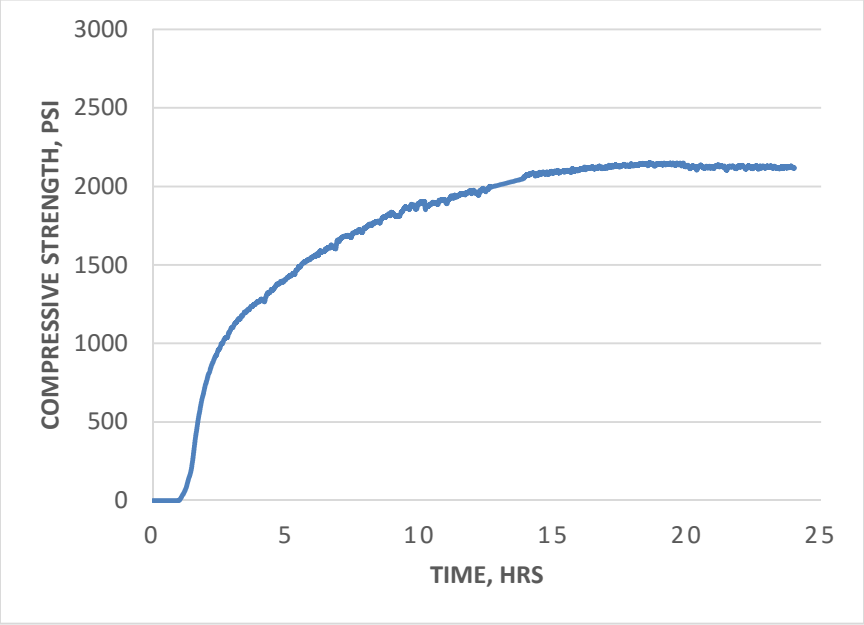

Figure 4-8: Compressive strength development of G3 slurry

Comparison of compressive strength development of class G slurry and all mixes with Nano zeolite revealed that G1 did not have higher compressive strength than G slurry. However, significant improvement in early strength was observed with G2 mix. Still, there was not much increase in the final 24 hours' strength. In G3 mix, early strength was reduced significantly as compared to other mixes. In early stage up to 12 hours, G2 mix shows the highest early strength. While the G1 shows the highest strength at 24 hours. Comparison of compressive strength values of all the mixes at different time intervals are presented in **Table 4-3** and **Figure 4-9**.

Table 4-3: Compressive strength results at different time durations

Time (HH:MM)	G (Psi)	G1 (Psi)	G2 (Psi)	G3 (Psi)
6:00	1730	1743	1983	1554
12:00	2170	2180	2312	1976
18:00	2320	2337	2444	2135
24:00	2430	2546	2500	2100

Time to achieve a compressive strength of 50, 500 and 2000 psi for slurries are summarized in **Figure 4-10, Figure 4-11** and **Figure 4-12**. Time to reach a compressive strength of 2000 psi is important, as this strength is considered safe for perforation or stimulation job. It is observed Nano zeolite slurries have low time required to reach 2000

psi strength as compared to neat class G cement. G2 slurry reached the 2000 psi strength in the shortest time. G3 slurry was the last to reach 2000 psi compressive strength.

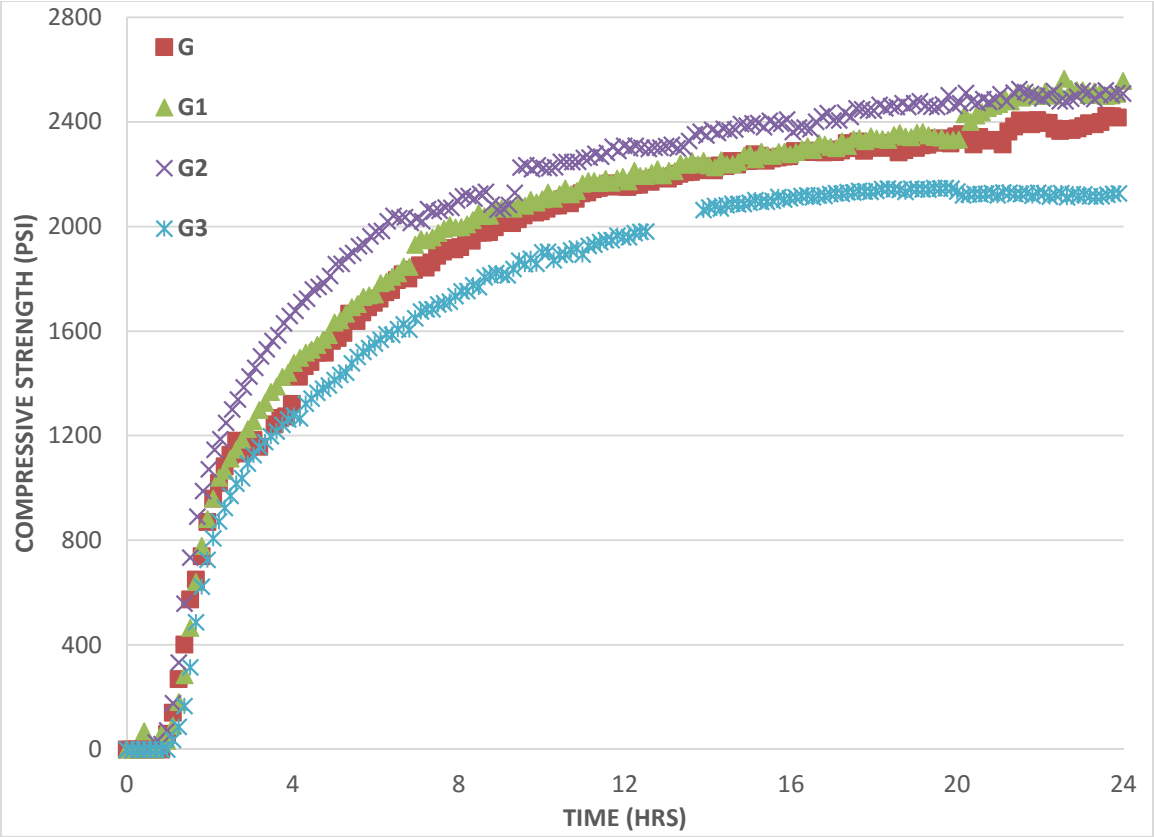

Figure 4-9: Compressive strength develpoment of Class G cement with different percentages of Nano zeolite

The transition period between developing a compressive strength of 50 psi and 500 psi is important and should be as short as possible to avoid long waiting time on cement before resuming drilling operation. **Figure 4-13** presented the effect of Nano zeolite on transition time from a strength of 50psi to 500psi. G2 slurry has the shortest transition time which might be helpful in reducing the wait on cement time.

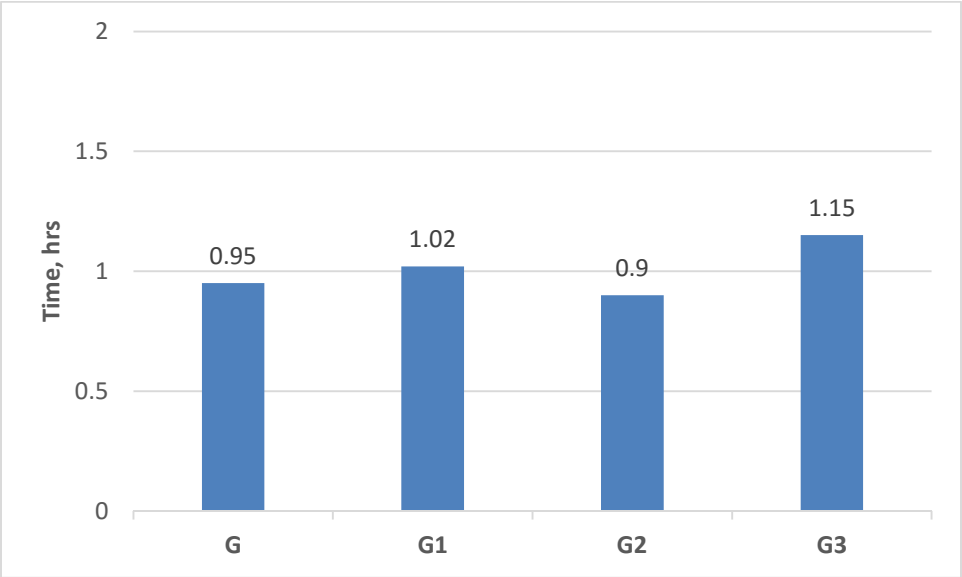

Figure 4-10: Time to gain 50 psi compressive strength

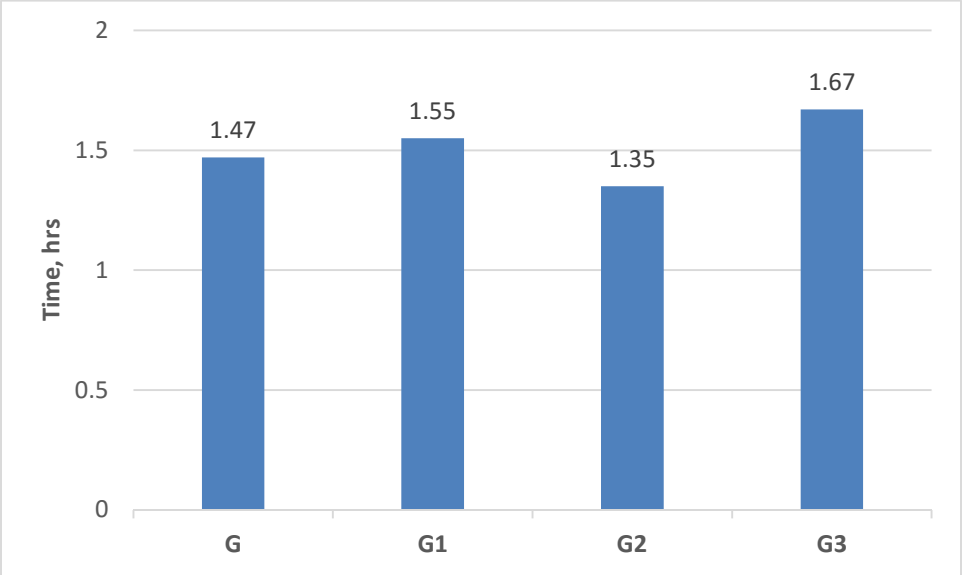

Figure 4-11: Time to gain 500 psi compressive strength

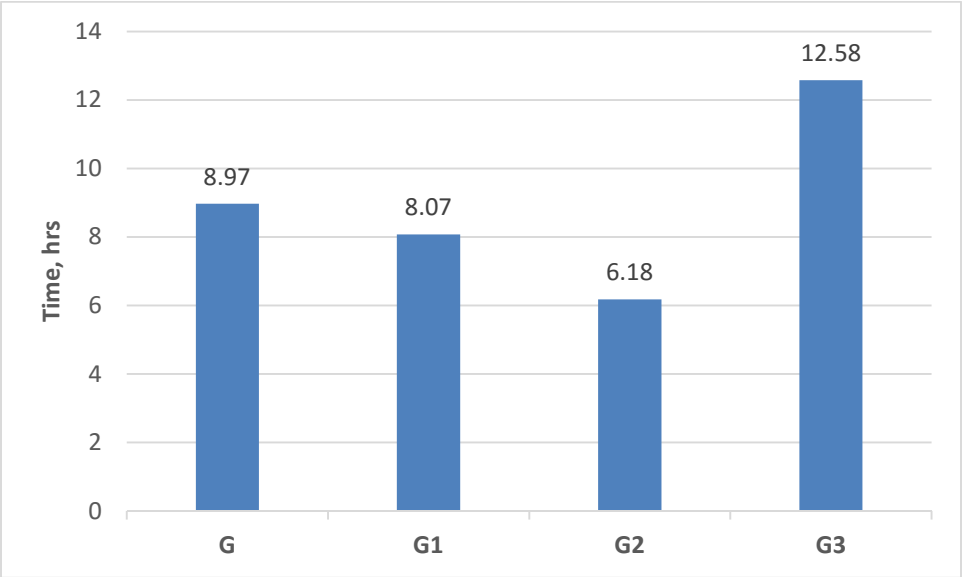

Figure 4-12: Time to gain 2000 psi compressive strength

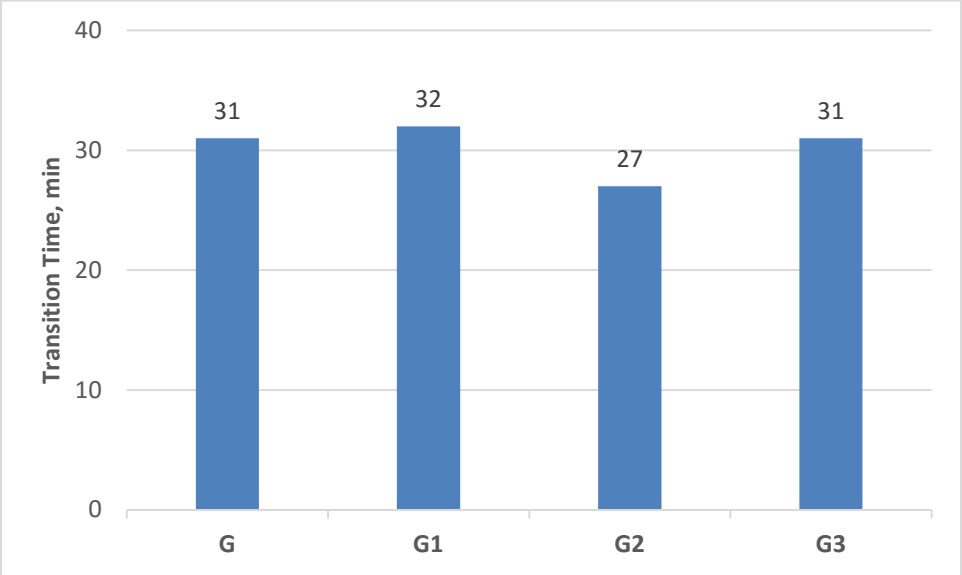

Figure 4-13: Transition time from 50psi to 500psi

4.5 EFFECT OF NANO ZEOLITE ON POROSITY AND PERMEABILITY

Addition of Nano zeolite decreased the porosity and permeability of set Class G cement slurry as shown in **Table 4-4** and **Figure 4-14**, **Figure 4-15**. Addition of Nano zeolite at 1% bwoc decreased the porosity and permeability significantly, up to 17% and 98% respectively. Porosity and permeability of G2 slurry was not included in figures because of erroneous results due to the breakage of core. Further increase in Nano zeolite concentration increased the porosity and permeability.

Table 4-4: Effect of Nano zeolite on porosity & permeability of Class G cement

Properties	G	G1	G2	G3
Porosity	25.76	21.48	28.654*	30.31
Permeability (md)	0.3263	0.0073	2.1054*	0.2984

* Core breakage

Porosity and permeability reduction confirmed the nanofillers effect of Nano zeolite as nanomaterial. Reduction in permeability is more significant as compared to porosity, this result is in line with the effect of Nano silica as reported by (Ershadi et al. 2011). Nanoclay has also been shown to reduce the permeability and porosity of set Class G cement (Murtaza et al. 2016).

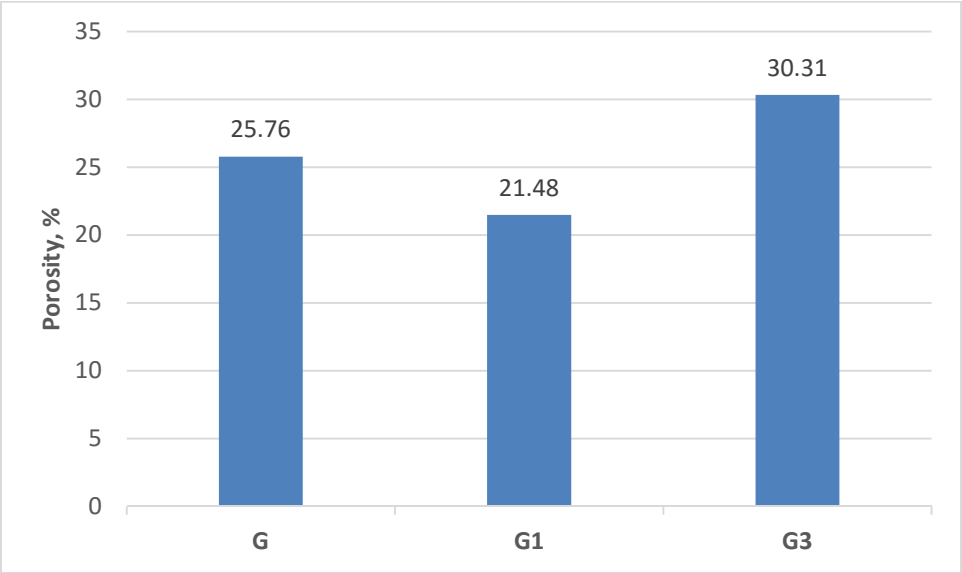

Figure 4-14: Porosity of class G cement with addition of Nano zeolite

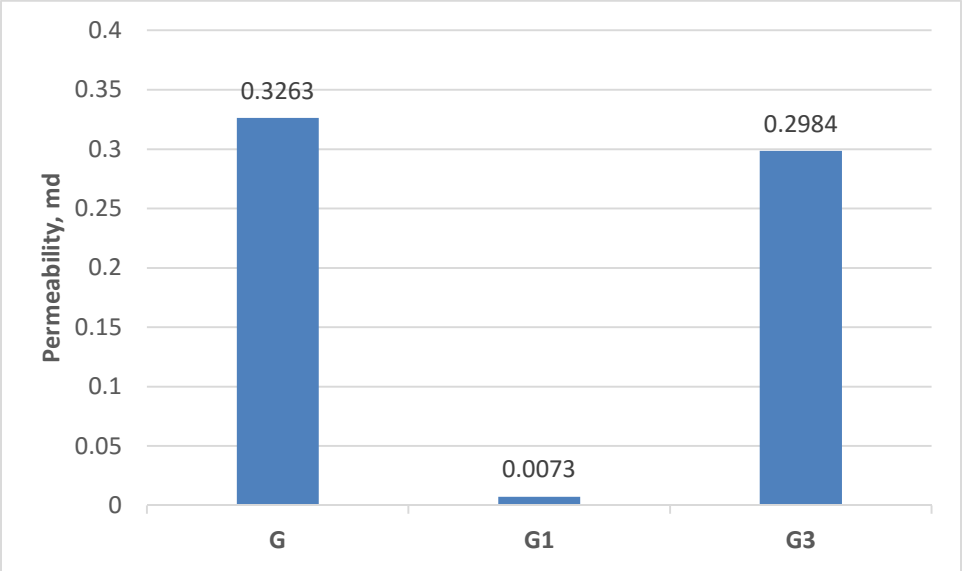

Figure 4-15: Permeability of class G cement with addition of Nano zeolite

4.6 MICROSTRUCTURAL ANALYSIS

Microstructural analysis, to understand the hydration products of different slurries, is performed to understand the compressive strength and porosity results. The hydration products and their structures affect the strength and porosity results (Bu et al. 2016). The hydration products of cement are dependent on the curing temperature. In the present study, cement samples are cured for 24 hours at 290°F and then XRD and SEM analysis' were performed.

The main phases present in hydrated cement paste microstructure at higher temperatures are calcium silicate hydrate gel CSH (II) [Ca2SiO4·3H2O], C2SH2[Ca2SiO4·2H2O] α-C2SH, calcium hydroxide CH[Ca(OH)2], Tobermorite, Ettringite Aft [3CaO·Al2O3·3CaSO4·32H2O] and Monosulfate Afm [3CaO·Al2O3·CaSO4·12H2O], unhydrated cement particles and air voids (Murtaza et al. 2016 and Mondal 2008). The main component of hydrated cement paste microstructure is CSH, which contributes to the mechanical properties (Franus, Panek and Wdowin 2015).

Effective dispersion to avoid nanoparticles agglomeration is the key in improving the microstructure of the cement with nanoparticles. Otherwise, inclusion of nanomaterials can negatively affect the cement properties. As the excess nanomaterials, can be agglomerated and produce weak zones affecting the strength significantly (Liu, Li and Xu 2015).

XRD is semi quantitative analysis, so the percentages given can be little inaccurate, but the trend will be according to the peaks of different crystalline materials observed in the mix. Hydration products of different cement mixes as estimated by XRD is shown in **Table 4-5**. It can be observed that the concentration of calcium silicate hydrate (CSH) reduced significantly and Portlandite (CH) increased in case of G3 slurry. CSH for G1 and G2 is higher than the G mix. These results are in line with the compressive strength results as presented in Section 4.4. Higher CSH concentration is correlated with higher strength and vice versa. Some unreacted Silica is also present in case of higher concentration of Nano zeolite.

Table 4-5: Comparison of hydration products of all G class mixes by XRD (Semi quantitative)

Hydration products	G	G1	G2	G3
Calcium Silicate Hydrate (CSH)	43%	50%	46%	15%
Calcium silicate (Larnite)	26%	24%	7%	24%
Calcium Hydroxide	19%	10%	28%	46%
Aluminum Calcium Iron Oxide (Ca_2FeAlO_5)	12%	16%	15%	10%
Silicon oxide (Quartz)	0%	0%	4%	5%

SEM image and EDS analysis for G slurry is shown in **Figure 4-16** and **Figure 4-17**. Microcracks are clearly visible in the images shown by arrows. EDS was performed at the location shown in square as Spectrum 1. This structure is believed to be the CSH (C/S = 2) which is confirmed by the EDS. CSH is also visible at other positions in the image,

which are marked as ‘1’. There are void spaces too which are visible as dark spaces and indicated as ‘2’.

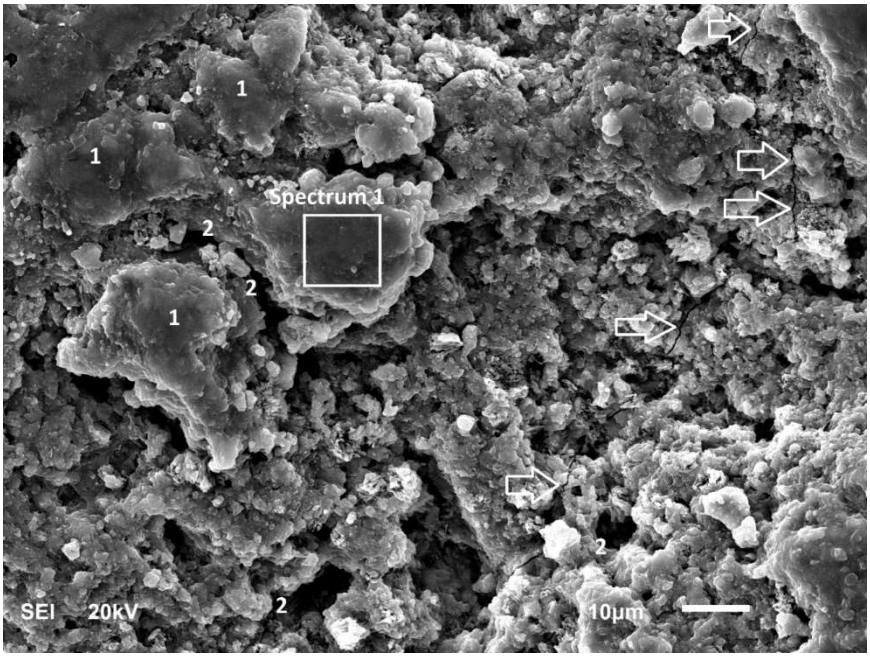

Figure 4-16: SEM image of set G mix cured at 290°F for 24 hours

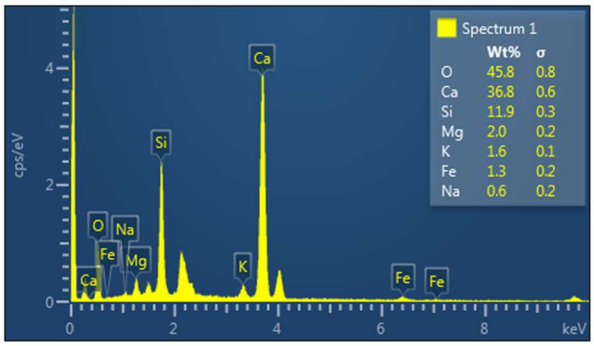

Figure 4-17: EDS results of spectrum 1 from G mix

Microcracks are visible in G1 as well, as indicated in **Figure 4-18** by arrows, although its less than G slurry mix. **Figure 4-19** and **Figure 4-20** are magnification of **Figure 4-18**, to

analyze the smaller particles, which appears to be unreacted Nano zeolite particles agglomerated in the mix. These particles are highlighted by white circle as can be seen in **Figure 4-19.**

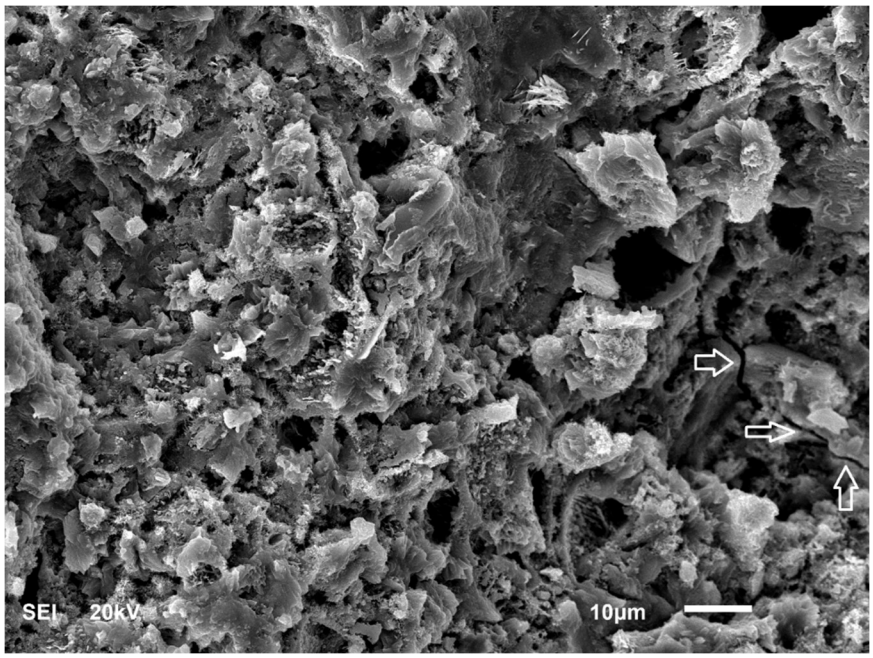

Figure 4-18: SEM of G1 mix cured at 290°F for 24 hours

Figure 4-20 shows the particle size of smaller particles as estimated by tool provided in EDS analysis software. The particle size of range 400-600nm can be seen. In addition, the SEM analysis of Nano zeolite gave similar particles of 400-600 nm indicating the agglomeration of particles (see **Figure 4-21**). Looking at the mix that only consists of Class G cement, Nano zeolite and water, it can be confirmed that these are unreacted particles of Nano zeolite.

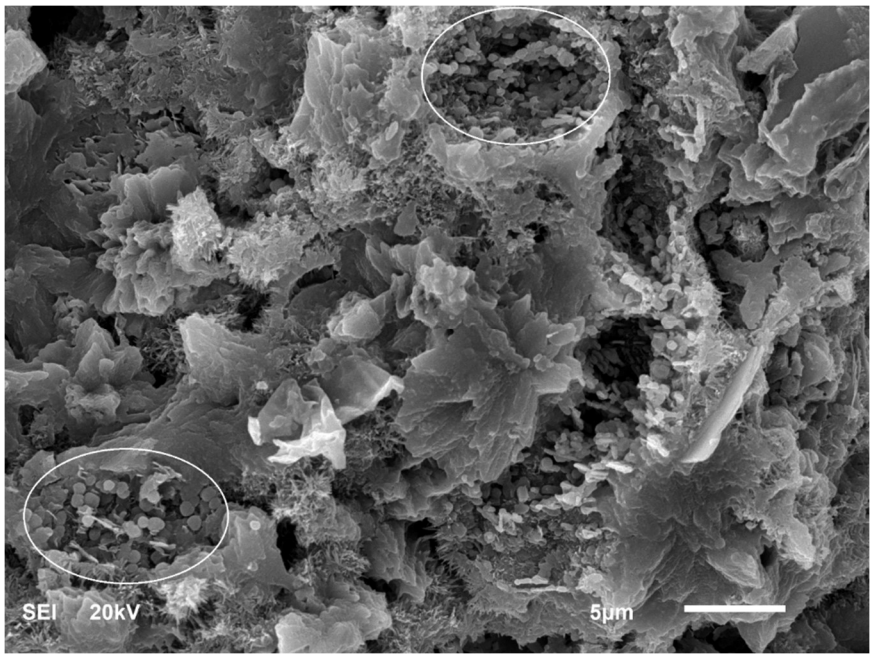

Figure 4-19: SEM of G1 mix cured at 290°F for 24 hours

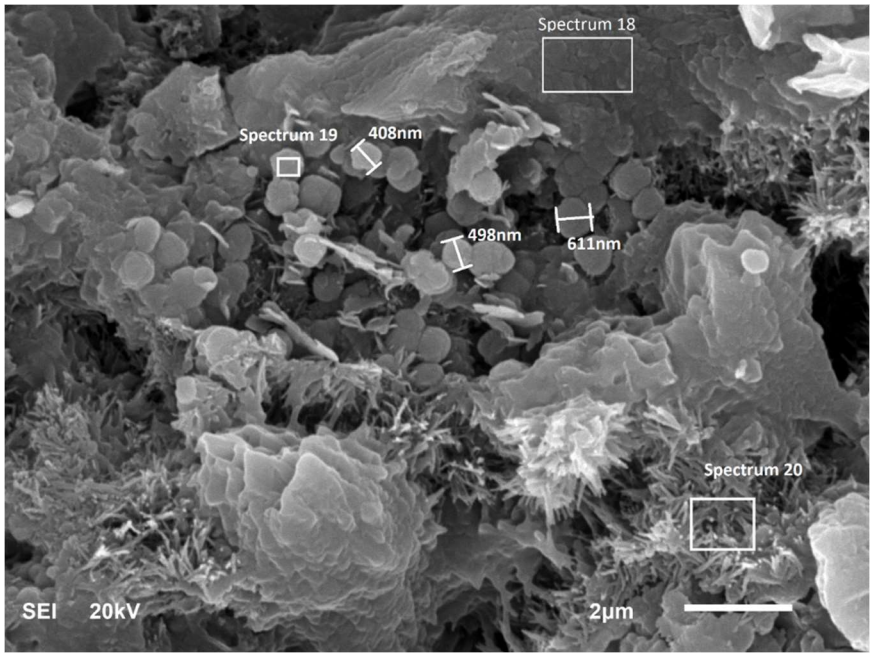

Figure 4-20: SEM of G1 mix cured at 290°F for 24 hours

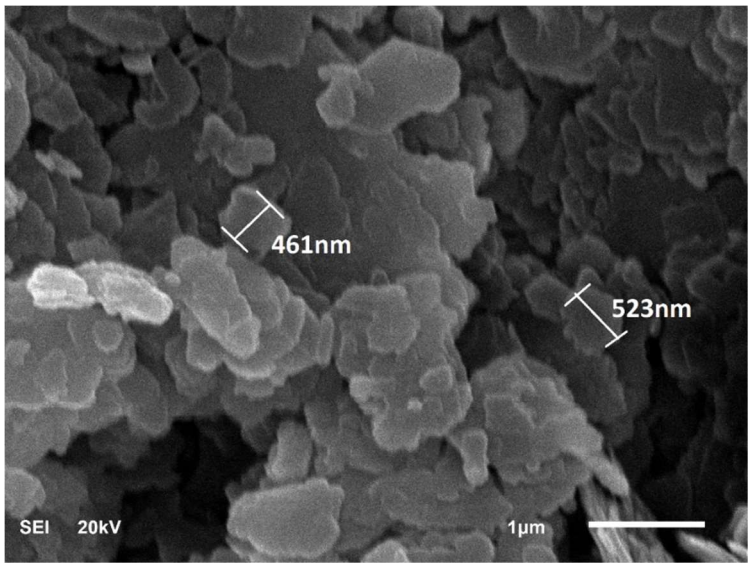

Figure 4-21: SEM image of Nano zeolite particles with size

EDS analysis at different locations is summarized in **Figure 4-22**. Location selected as Spectrum 18 indicates the high dense CSH which is also called as inner product, EDS analysis shows the presence of silica with C/S = 3.5. On the other hand, Spectrum 20 shows the needle like, low dense CSH, which is termed as outer product CSH. EDS analysis indicated the C/S ratio of 3.25. It appears that Nano zeolite particles are filling the pore space between both type of CSH.

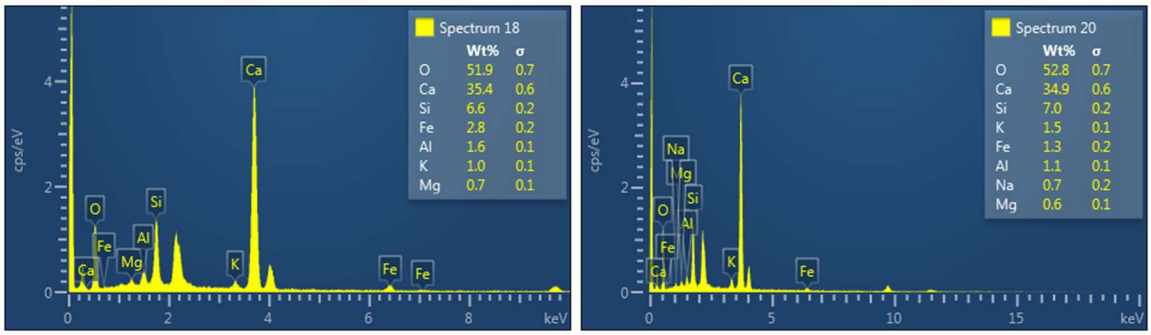

Figure 4-22: EDS results of spectrum 18 and 20 from G1 mix

SEM analysis of G2 mix is presented in **Figure 4-23** and **Figure 4-24**. From **Figure 4-23**, it is evident that no micro cracks were visible in G2 mix unlike G and G1. G2 appears to be the denser mix among all. Hydration products were further modified with the increase in Nano zeolite concentration.

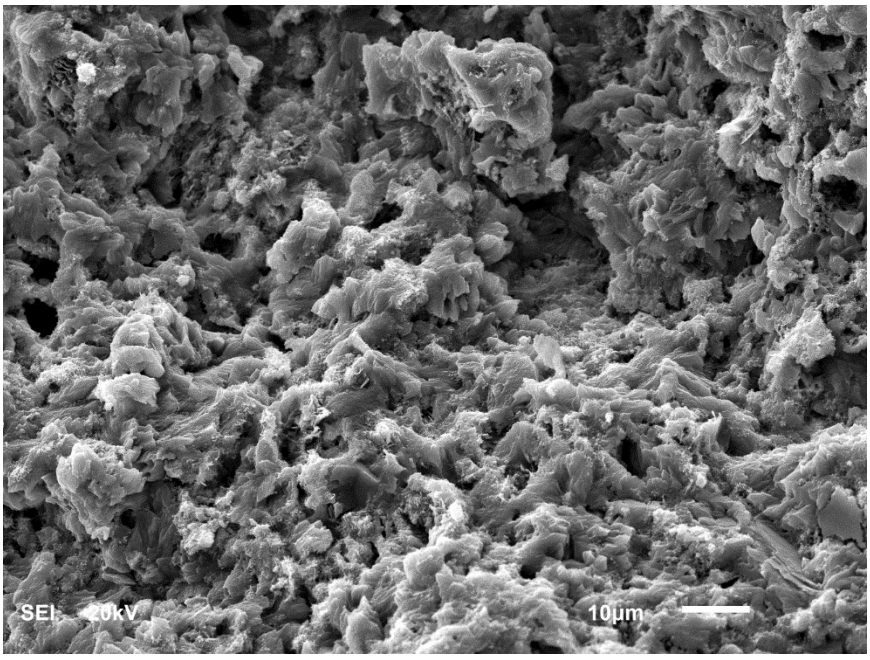

Figure 4-23: SEM of G2 mix cured at 290°F for 24 hours

From **Figure 4-24**, it can be observed that there are some unreacted Nano zeolite particles left in the mix like G1 as highlighted by white circles. However, the amount of unreacted particle is very less in G2 mix. It appears that the Nano zeolite particles acted as nucleation sites on which outer CSH particles grew. Magnified image at the same area is presented in **Figure 4-25**, which confirms the observation of Nano zeolite acting as the nucleation site. Nano zeolite particles connected with growth of CSH can be seen in the image. After the comparison of compressive strength results of G1 and G2 slurry, it is

revealed that the final strength at 24 hours is same but the enhancement in early strength is significant in case of G2. This observation also validates the nucleation sites phenomenon as observed in SEM images.

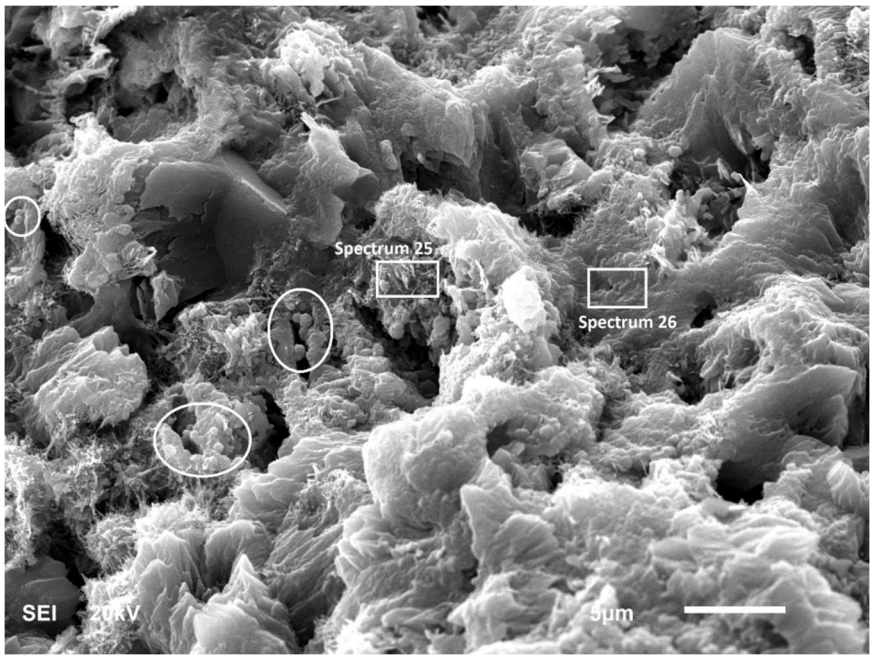

Figure 4-24: SEM of G2 mix cured at 290°F for 24 hours

EDS analysis at different locations of **Figure 4-24** is summarized in **Figure 4-26**. Location selected as Spectrum 25 indicates the low dense CSH on which the EDS analysis shows the presence of CSH with C/S = 1.45. On the other hand, Spectrum 26 shows the compact, dense, inner product CSH, with the C/S ratio of 2.45 confirmed by EDS analysis.

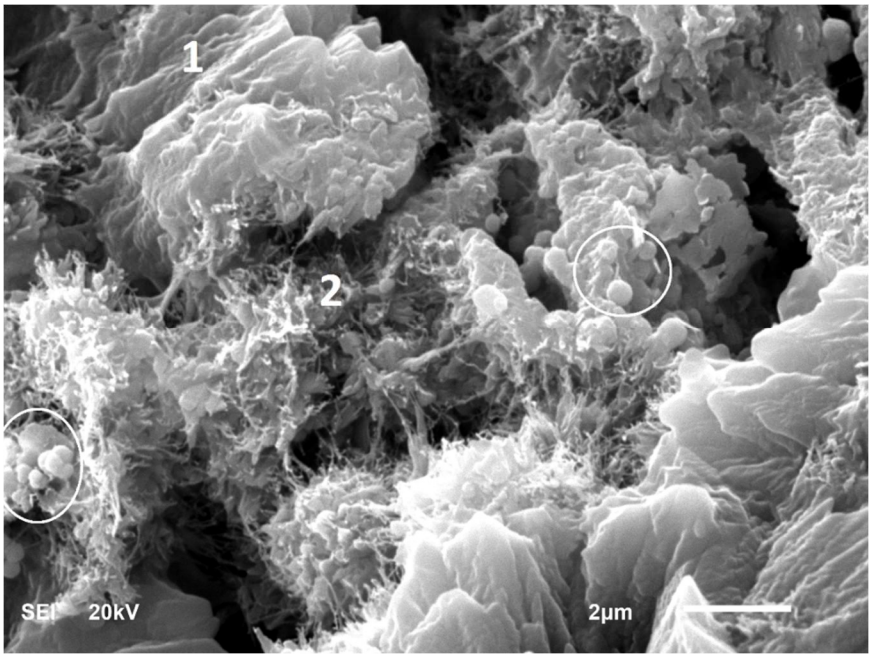

Figure 4-25: Magnified SEM image of G2 mix cured at 290°F for 24 hours

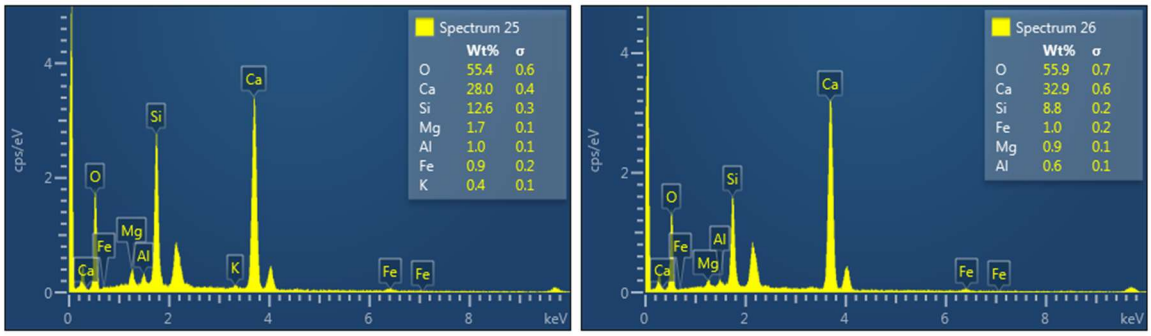

Figure 4-26: EDS results of spectra 25 and 26 from G2 mix

SEM and EDS analysis of G3 mix is presented in **Figure 4-27**, **Figure 4-28**, **Figure 4-29** and **Figure 4-30**. The microstructure observed in G3 slurry is completely different from what was seen in other G mixes. From **Figure 4-27**, it can be observed that 3 different types of structure are seen in the mixture.

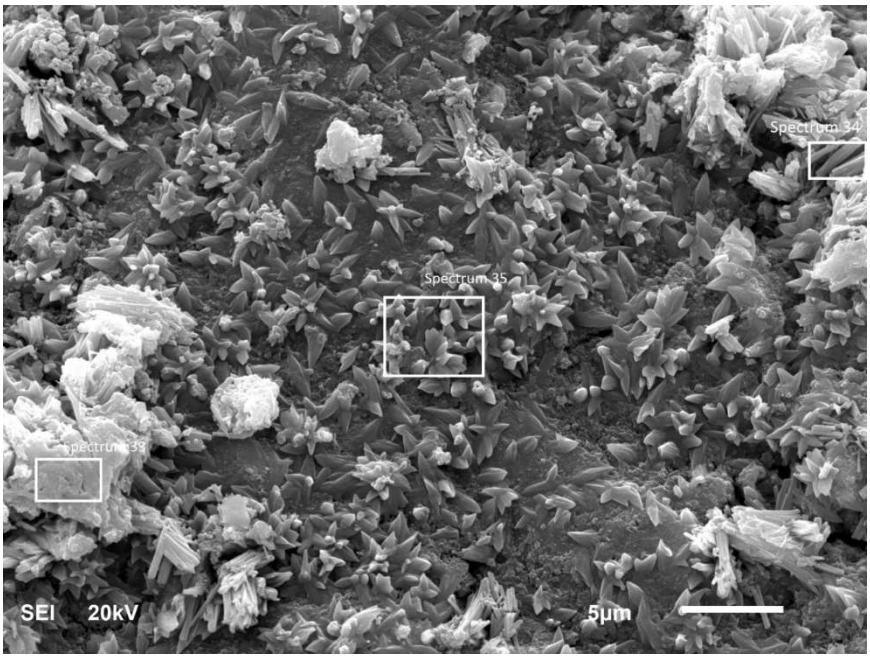

Figure 4-27: SEM of G3 mix cured at 290°F for 24 hours

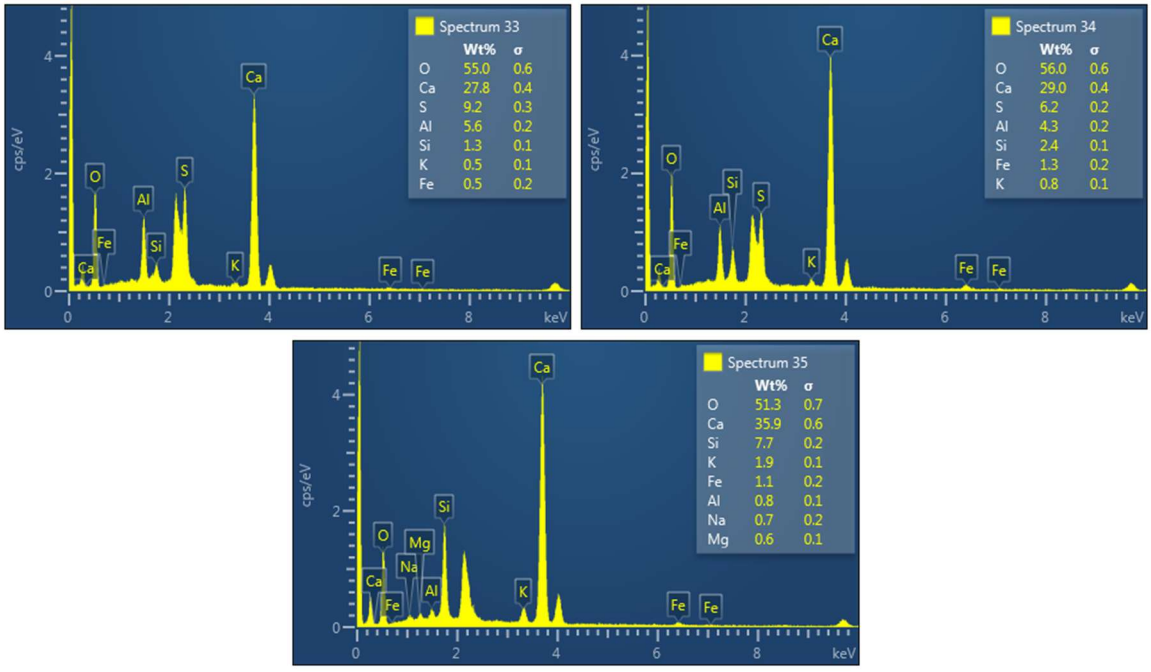

Figure 4-28: EDS results of Spectra 33, 34 and 35 from G3 mix

One flower like structure, which is widely spread in the mixture, captured by spectrum 35. Rod like structure, which is clear in Spectrum 34, and spectrum 33, which appears to be agglomeration of rod like structure. EDS analysis of these structures is shown in **Figure 4-28**. Rod like structure is shown to be rich in Sulphur and Aluminum, which is perceived as kind of Ettringite or Monosulfate. Significant decrease of G3 mix compressive strength also confirms the formation of sulfate. These results can also be validated by the porosity and permeability results that showed significant increase as compared to G1 slurry. EDS of flower like structure revealed some form of CSH with C/S ratio of 3. Magnified SEM image at the same location is presented in **Figure 4-29**. Beside flowery and rod like structure, a dense CSH microstructure can be seen. EDS analysis in **Figure 4-30** confirmed the C/S ratio of 1.82.

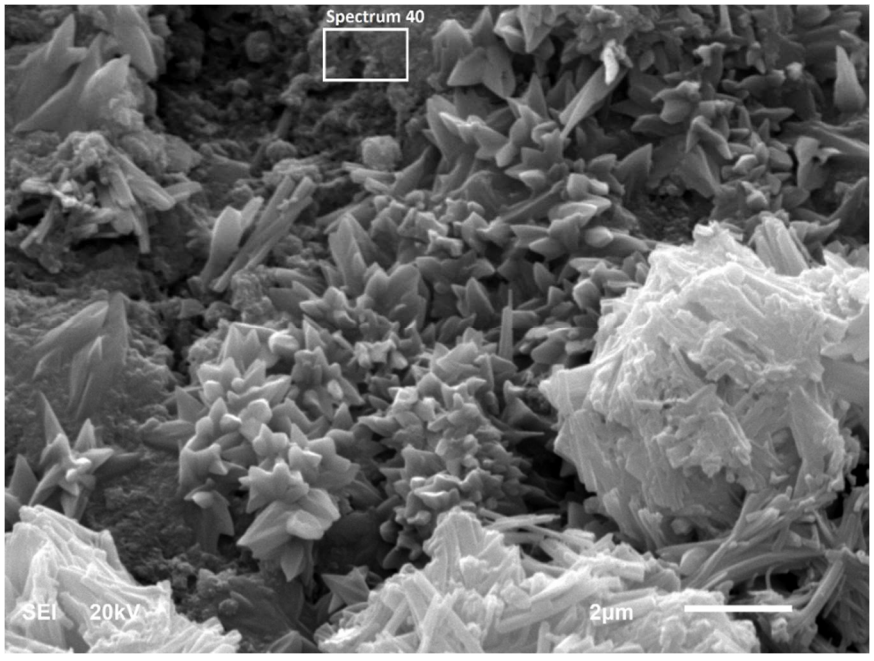

Figure 4-29: SEM of G3 mix cured at 290°F for 24 hours

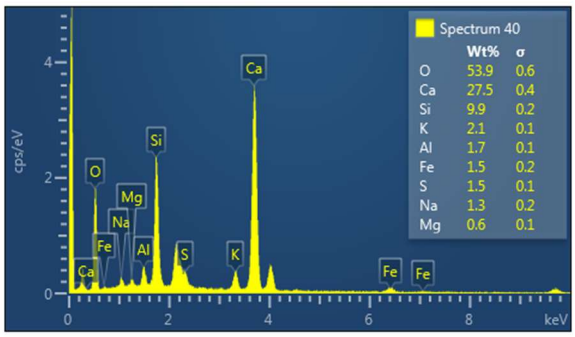

Figure 4-30: EDS results of Spectrum 40 from G3 mix

To summarize the results of microstructural analysis, following conclusions can be made:

- Addition of Nano zeolite modified the cement hydration products as compared to the neat Class G slurry.
- From the SEM images of G and G1 cement slurries, micro cracks are evident which can be attributed to the strength retrogression at high temperatures. However, as the concentration of Nano zeolite increased, no micro crack was observed.
- Both inner product and outer product CSH (high dense and low dense) were observed in G1 mix implying the effect of Nano zeolite particles on cement hydration.
- From SEM image of G1, agglomeration of nanomaterial can be seen in pore spaces, which is confirming the Nano filler effect of Nano zeolite. Porosity and permeability results also validated the Nano filler effect, as G1 decreased porosity and permeability values significantly.

- In addition, it can be observed that there is a need of effective dispersion of Nano zeolite particles as many particles are agglomerated in some pore spaces leaving other pore spaces open. This explains why significant reduction in porosity and permeability did not convert to higher compressive strength.
- It also shows the lack of reactivity of Nano zeolite particles in G1 mix as it can be observed the unreacted particles of Nano zeolite present in the mix. On the contrary, G2 mix has lesser amount of unreacted NZ particles.
- Inner and outer product CSH can be observed in G2 mix which as well implies the growth of CSH on NZ particles. It can also be endorsed by the acceleration of compressive strength at early time with NZ addition.
- G3 mix shows elongated structure, which is rich in Sulphur and Aluminum and it appears to be Monosulfate (afm) or Ettringite (aft). At some locations, CSH is also seen with lower CSH ratio, but only a few locations.
- It is important to note that XRD with G3 gave low CSH content, which appears to be confirmed by the SEM results.
- In G3 mix, one of the possible explanations of lower strength might be that Nano zeolite in higher concentration increased the amount of Alumina in the mix which reacted with sulfate to form some form of Ettringite or Monosulfate.

CHAPTER 5

EXPERIMENTAL INVESTIGATION OF NANO AND MICRO ZEOLITE WITH CLASS G CEMENT AND ADDITIVES

This chapter describes the results of study on the effect of Nano and micro zeolite on API type 'G' cement properties. The results of laboratory tests at various concentrations of zeolites are discussed here along with the base mix results for comparison.

5.1 CEMENT SLURRY DESIGN

The chosen well has a special cement system design since this well is 14,000 ft deep with high pressure and temperature conditions. The selected cement system consists of different materials in which each material contributes and adds chemical and physical property to make the cementing job successful.

All the cement properties explained earlier in the introduction are estimated for the cement design presented in **Table 5-1**, which will be termed as base mix slurry to be used for reference. After the completion of experiments with base cement slurry, Nano and

micro zeolite were incorporated in the above cement slurry design in different concentrations by weight of cement (BWOC).

Table 5-1 : Cement slurry design without Zeolites

Mix Design Label	**BM**
Properties	**Values**
Slurry density (Approx.), ppg	16.71
Water Cement Ratio (WCR)	0.44
Slurry yield	1.367
Class G cement powder + 35% Silica flour + 1% Expanding agent + 1% Dispersant + 0.2% Fluid loss control agent + 0.5% Fluid loss control agent + 0.7% Retarder + 0.25gm Defoamer	

Table 5-2 explains the cement slurry design in the presence of Zeolites. All the additives concentration is kept same in all mixes as base mix; only concentration of Zeolites is modified as explained in the table.

Table 5-2 : Cement slurry design with Zeolites

Component	**Mass (percentage by weight of cement)**				
Mix design label	BM	NZ1	NZ2	NZ3	MZ1
Micro zeolite	0	0	0	0	1
Nano zeolite	0	1	2	3	0

5.2 EFFECT OF NANO AND MICRO ZEOLITE ON THICKENING TIME

Thickening time test determines the time in which slurry remains pumpable. This test was conducted using HPHT consistometer per API specifications (2012). The pressure was set at 9400psi and the temperature at 228°F. The time for heating rate was 49 minutes.

Figure 5-1, **Figure 5-2**, **Figure 5-3**, **Figure 5-4** and **Figure 5-5** show the thickening time results of base mix, Nano zeolite and micro zeolite slurries.

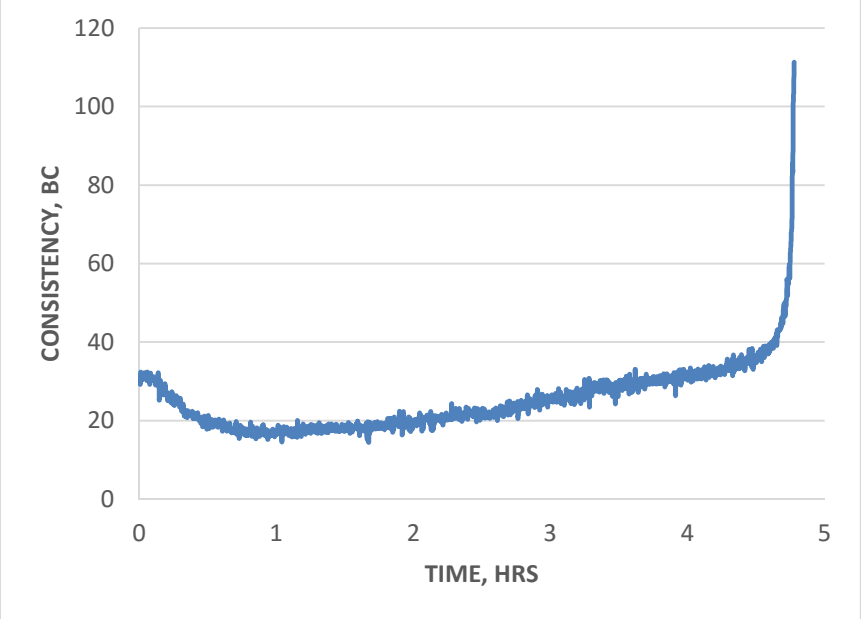

Figure 5-1: Thickening time plot of BM

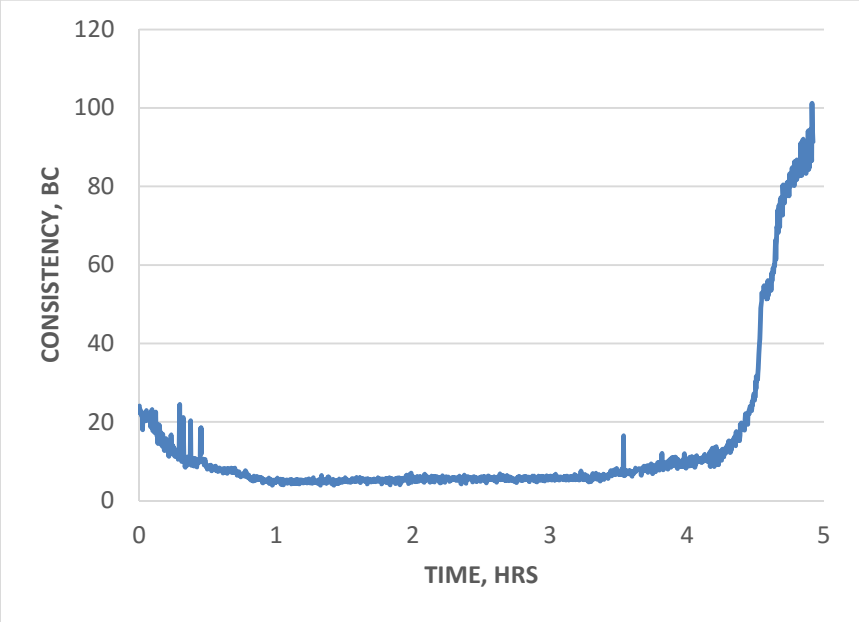

Figure 5-2: Thickening time plot of NZ1

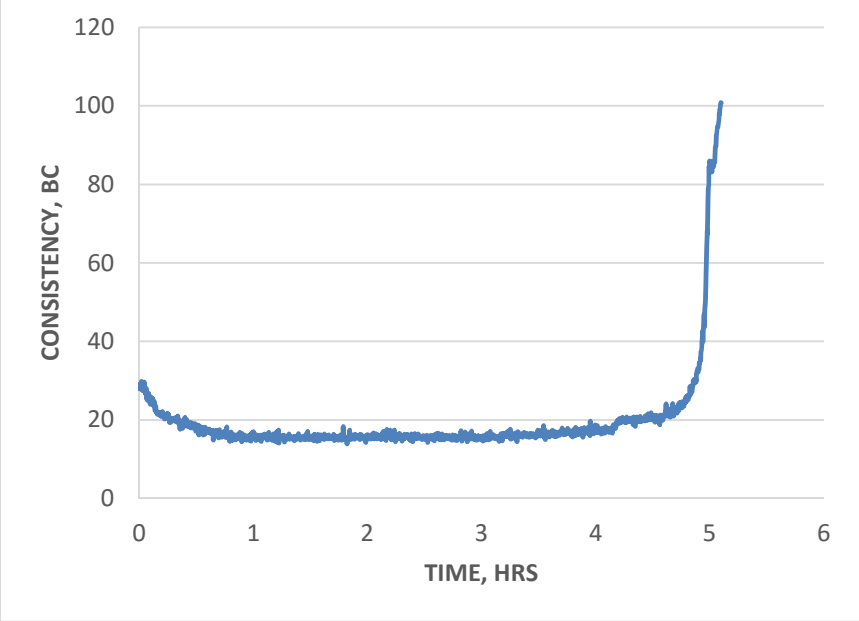

Figure 5-3: Thickening time plot of NZ2

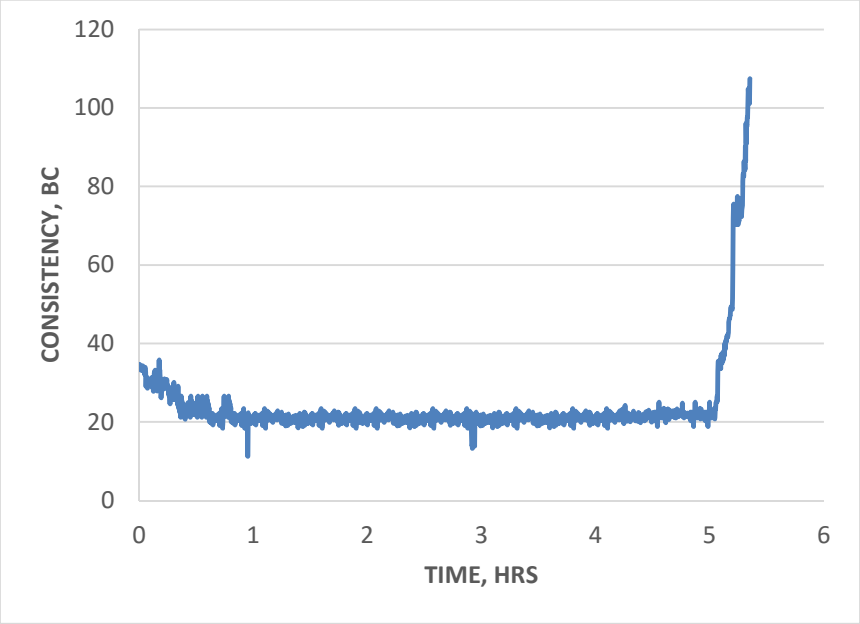

Figure 5-4: Thickening time plot of NZ3

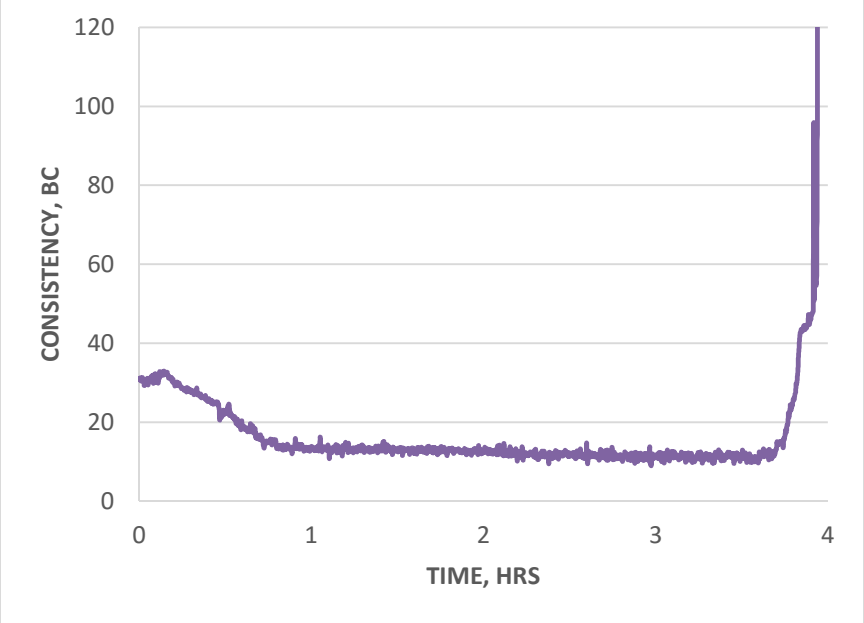

Figure 5-5: Thickening time plot of MZ1

From **Figure 5-6**, it can be observed that addition of Nano zeolite did not affect thickening time significantly, only a slight increase in thickening time was observed. This indicates the compatibility of Nano zeolite with retarder used (HR12). On the other hand, it can be observed that addition of micro zeolite resulted in a decrease in thickening time. So, thickening time required for specific job can be obtained by changing the concentration of retarder.

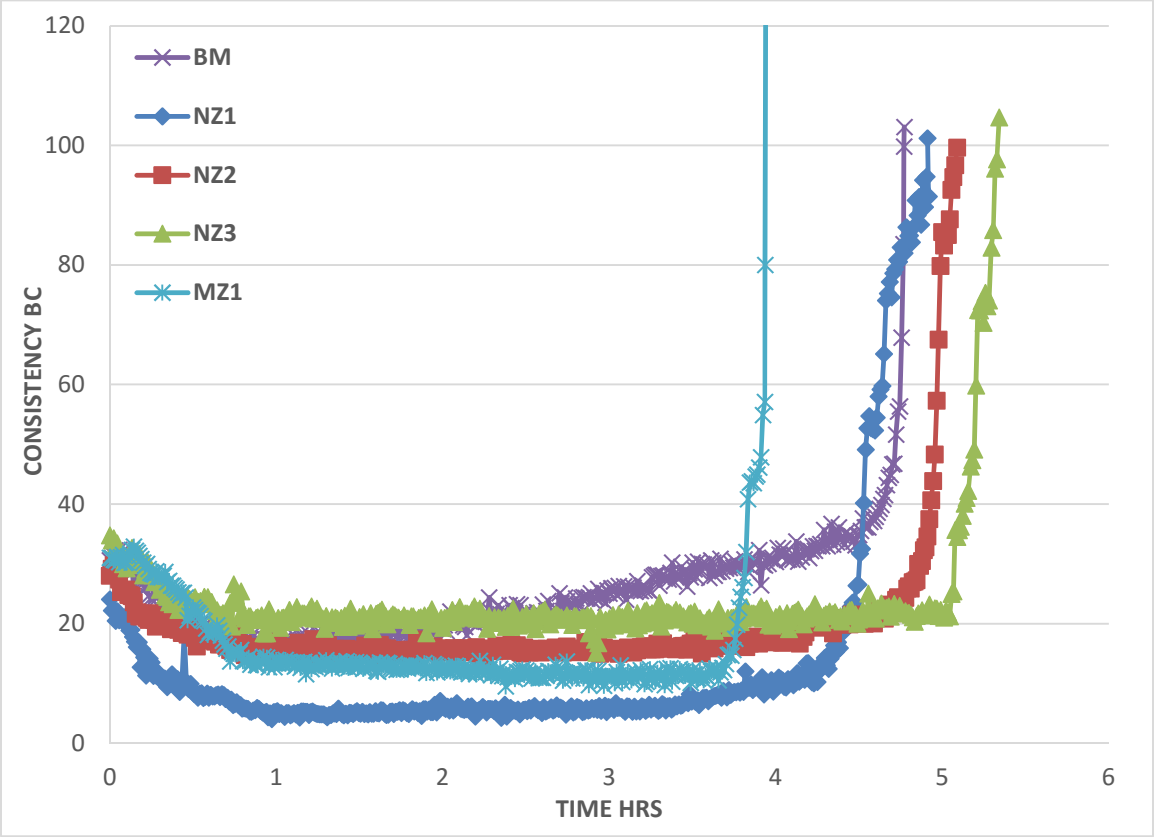

Figure 5-6: Variation of thickening time at different zeolite concentrations

In **Figure 5-7**, consistencies at the start of the test are recorded. This is an indication of the viscosity of the cement slurry at the start of the test. It can be observed that initial

viscosity increased with the increase in Nano zeolite. Initial viscosity with micro zeolite appears to be unchanged. Maximum consistency during the 15 to 30 minutes' period after the initiation of the test was recorded to be less than 30 BC for all tests.

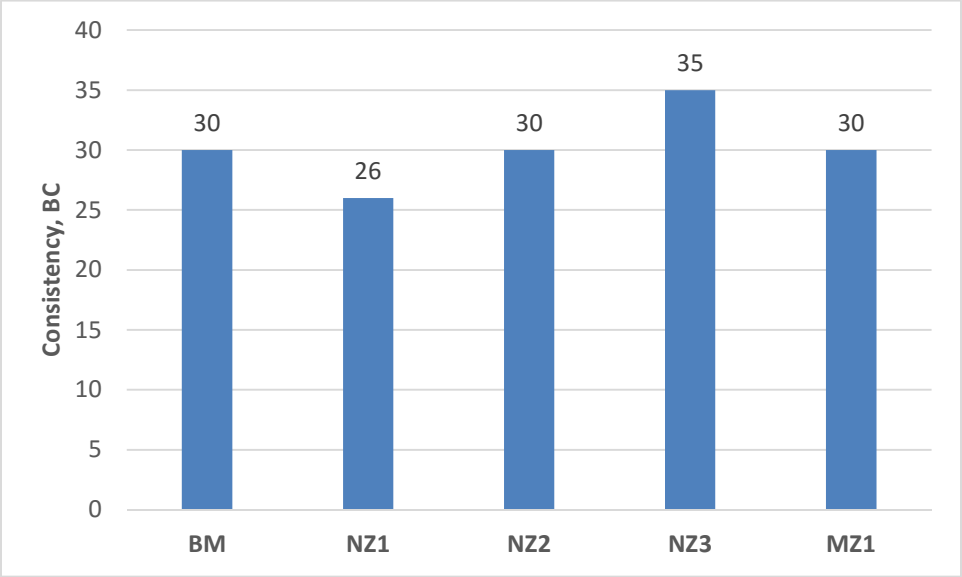

Figure 5-7: Consistencies at the start of the test

In **Figure 5-8**, time to reach 40 BC, 70 BC and 100 BC for base and zeolite slurries is shown. When all slurries approach 70Bc then time to get 100Bc is very short in all cement mix. This point is called right angle set as it takes minimum time to reach 100Bc consistency. Therefore, it can be concluded that 70Bc is point after which slurries can be considered unpumpable because there is short time span between 70Bc and 100Bc.

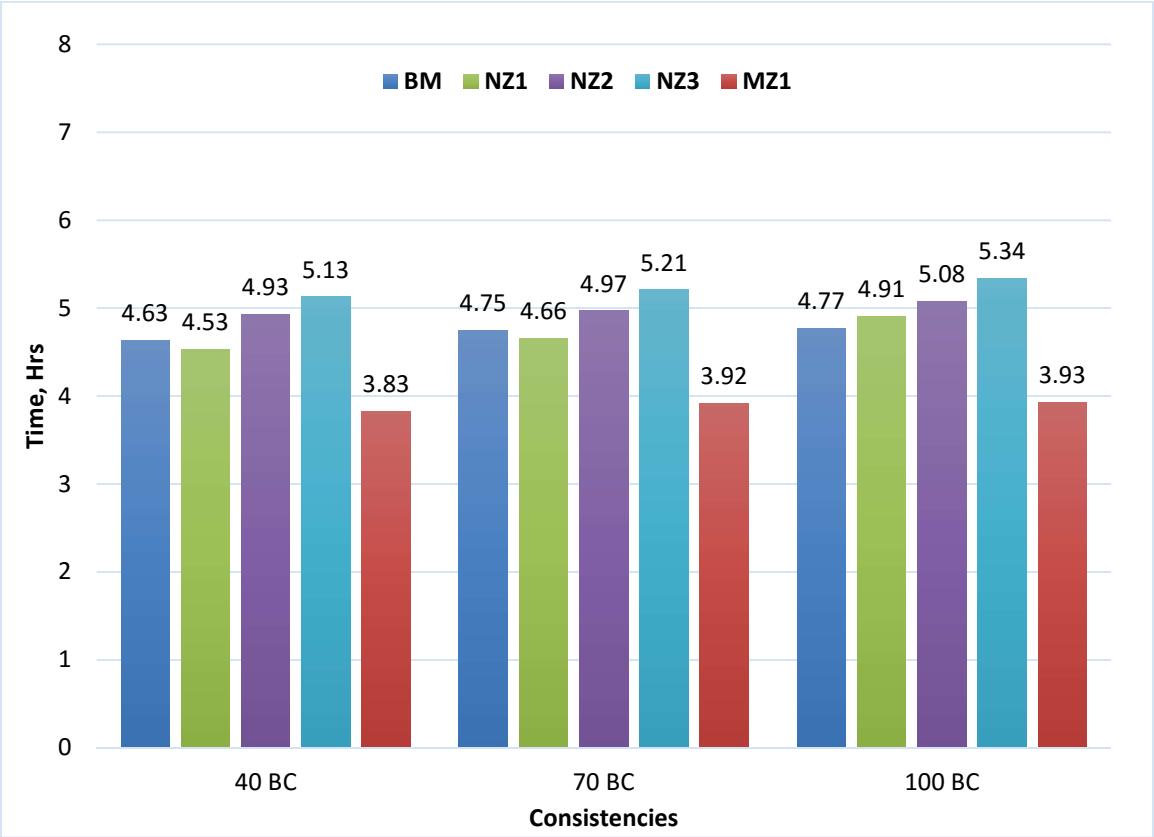

Figure 5-8: Time to reach 40BC, 70BC and 100BC consistencies

5.3 EFFECT OF NANO AND MICRO ZEOLITE ON DENSITY

Density of the cement slurry is selected based on pore pressure and fracture pressures of the formations to be cemented. In addition, it must be optimized for effective displacement of drilling fluid. The density of the cement slurry is usually measured by pressurized mud balance in the laboratory. The cement slurry is designed with reference of 16.71 lb/gal cement slurry of the selected well. The zeolite admixed cement slurries are subjected to density measurements. The densities of five cement slurry systems BM, NZ1, NZ2, NZ3 and MZ1 are measured in the laboratory (See **Table 5-3**).

Table 5-3: Density variation with addition of Zeolites

Cement Slurries	BM	NZ1	NZ2	NZ3	MZ1
Density (ppg)	16.8	16.95	16.85	16.9	17

The density of cement slurry can be controlled by either water cement ratio or weighing agents. The density of base mix is calculated to be 16.8 lb/gal. It is observed that both Zeolites did not increase base mix density significantly, that allows the cement slurry to be in the range of required density for specific jobs. This property is helpful in HPHT wells as in most of the cases the pore pressure and fracture pressure window is too small to operate. It should also be noted that density values reported here might be subjected to human measurement skills or the calibration accuracy of the balance.

5.4 EFFECT OF NANO AND MICRO ZEOLITE ON FREE WATER CONTENTS

Free water is water that might be separated from the cement slurry and accumulated at top of cement, which can result in particles settling effect. To determine the effect of Nano and micro zeolite on the amount of free water of cement slurry, base mix and all zeolite slurries have been aged for 2 hours under normal room temperature and atmospheric pressure in 250 ml graduated cylinder. Results are tabulated in **Table 5-4**. Results indicate that both Nano and micro zeolite did not cause any free water separation.

Table 5-4: Variation of free water contents of cement slurries with Zeolites

Cement Slurries	BM	NZ1	NZ2	NZ3	MZ1
Free Water (ml/250ml)	0	0	0	0	0

5.5 EFFECT OF NANO AND MICRO ZEOLITE ON RHEOLOGY

The rheological properties of an Oil-well cement (OWC) slurry defines the quality of the final product and assists predicting its end use performance and physical properties during and after processing. Rheological measurements determine the flow properties of the cement slurry such as plastic viscosity, yield point, gel strength, etc. Rheological properties variation with the addition of Nano and micro zeolite is presented in **Table 5-5**.

Table 5-5: Rheology of Nano and micro zeolite admixed cement slurries

Properties	BM	NZ1	NZ2	NZ3	MZ1
Plastic Viscosity (cp)	232	264	272	275	273
Yield Point ($lb_f/100ft^2$)	4	4	4	7	6

Addition of Nano zeolite and micro zeolite resulted in slight increase in plastic viscosity (see **Figure 5-9**) which is believed to be because of increase in solid particles. Increase in plastic viscosity may help in effective displacement of drilling fluids.

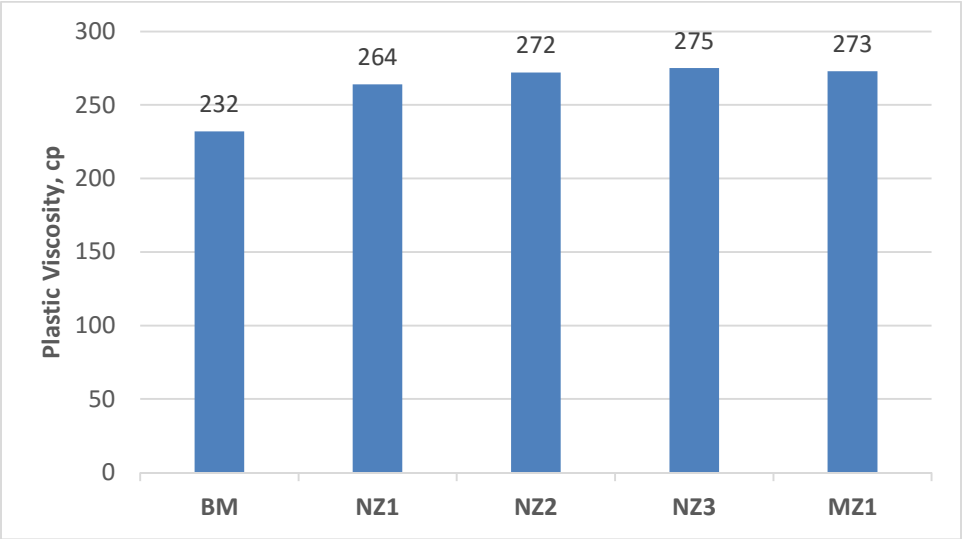

Figure 5-9: Plastic viscosity variation for different concentrations of Zeolites

Yield Point was not affected significantly as presented in **Figure 5-10**. It is desirable for the cement slurry to have low yield points.

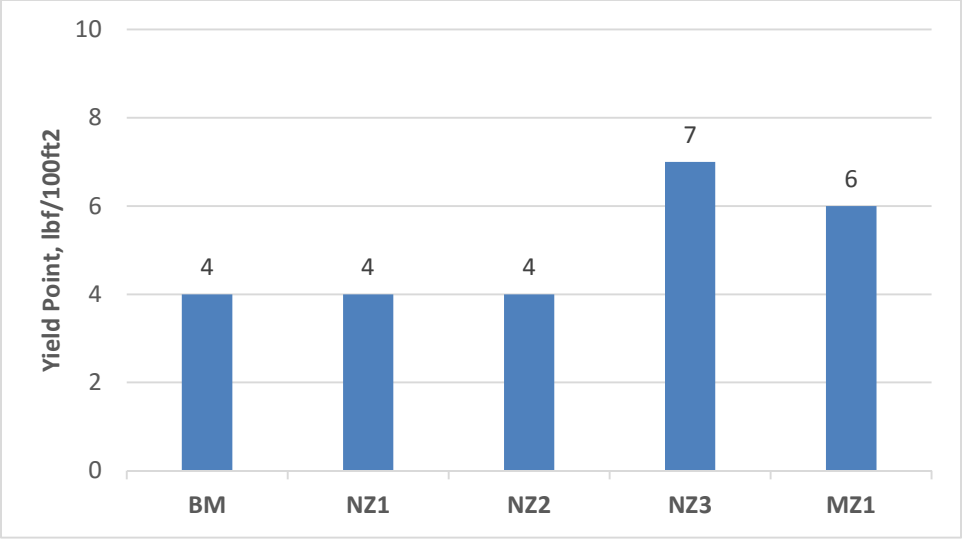

Figure 5-10: Yield point variation for different concentrations of Zeolites

Later, all cement systems are subjected to gel strength tests, which is measure of the attractive forces in particles that cause the development of gelation when flow is stopped. It also explains the force required to initiate the flow after stopping circulation. Effect of gel strength is summarized in **Figure 5-11** and **Table 5-6**. Both Nano and micro zeolite slurries improved gel strength, which indicate better particles suspending ability of cement slurries with zeolites.

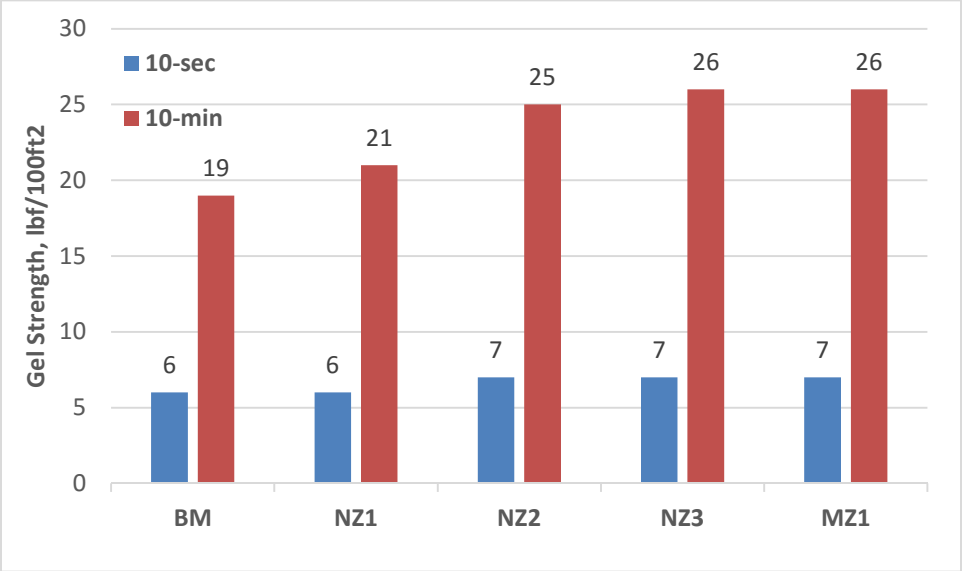

Figure 5-11: Effect of Zeolites on gel strength

Table 5-6: Gel strengths result of base mix and zeolite admixed slurries

Gel Strength ($lb_f/100ft^2$)	BM	NZ1	NZ2	NZ3	MZ1
10-sec	6	6	7	7	7
10-min	19	21	25	26	26

5.6 EFFECT OF NANO AND MICRO ZEOLITE ON COMPRESSIVE STRENGTH

The compressive strength measures the integrity and stability of cement to sustain long term imposed stresses. Cement slurry is supposed to develop the compressive strength early and make strong bond with walls of well after the placement. So, the drilling operations can be resumed in short time. The pumping of cement efficiently, placing it safely on time, assuring cement integrity after placement (prior to resuming drilling operation) are all issues to be considered. Therefore, compressive strength tests are conducted to evaluate the development of cement strength with time utilizing the ultrasonic cement analyzer (UCA) and to determine cement-bonding stability after set utilizing the conventional compressive strength test (crushing).

5.6.1 Effect of Nano And Micro Zeolite on Compressive Strength by UCA

The base mix and zeolite slurries have been subjected to the UCA test conducted under temperature 290°F and pressure 3000 psi for 48 hours. Sample chart of compressive strength development for base mix is shown in **Figure 5-12**. Compressive strength results are presented in **Figure 5-13**, **Figure 5-14**, **Figure 5-15**, **Figure 5-16** and **Figure 5-17**.

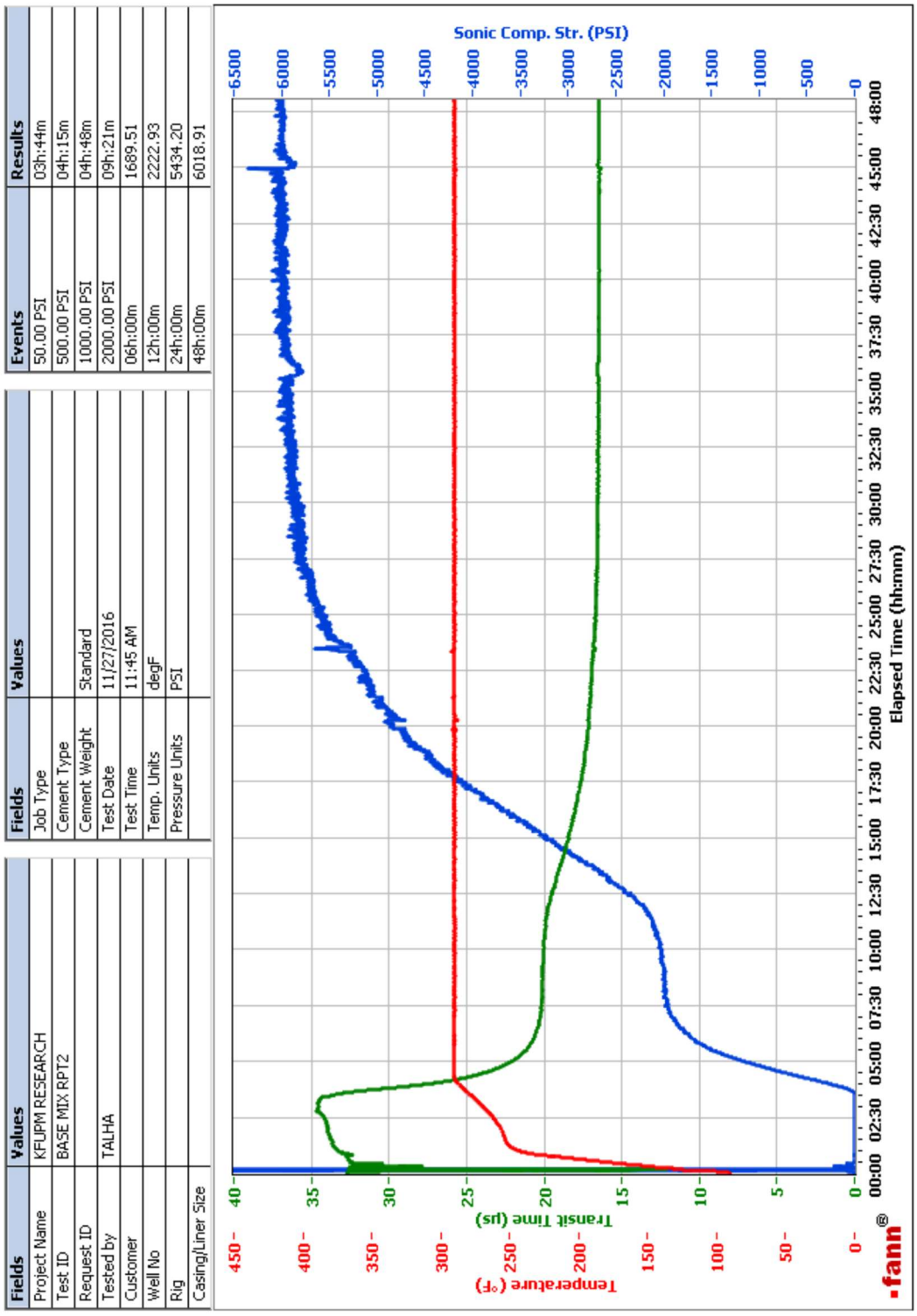

Figure 5-12: UCA sample chart as produced from UCA software for G2 slurry

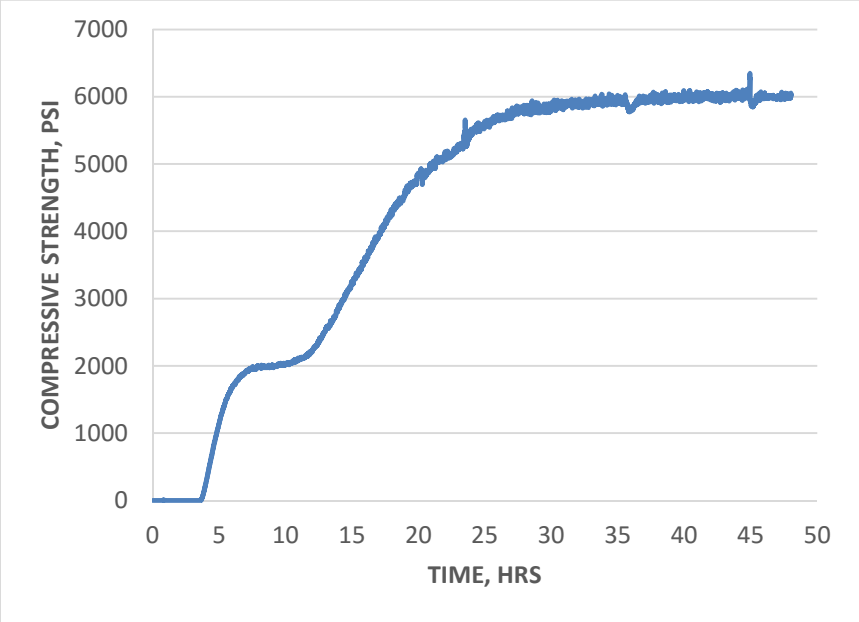

Figure 5-13: Compressive strength development of BM slurry

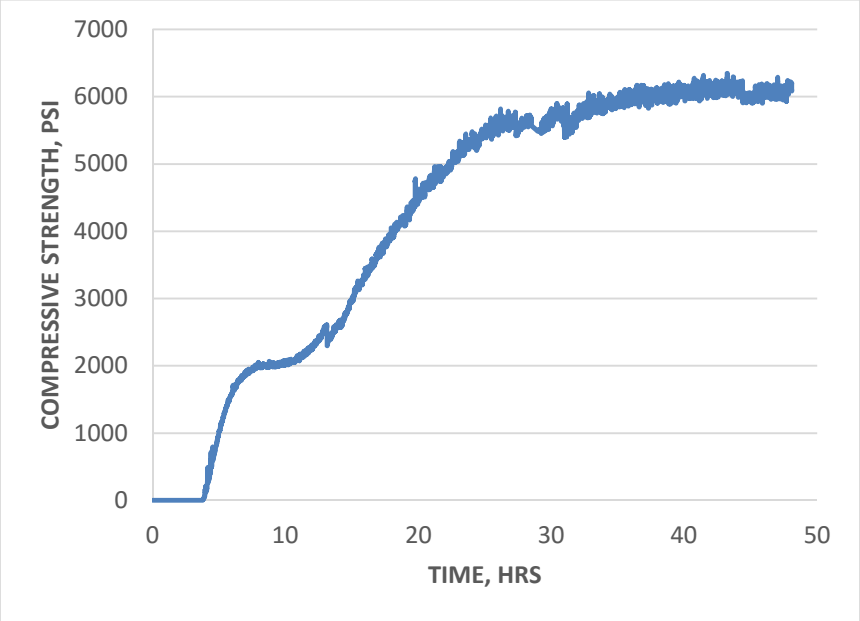

Figure 5-14: Compressive strength development of NZ1 slurry

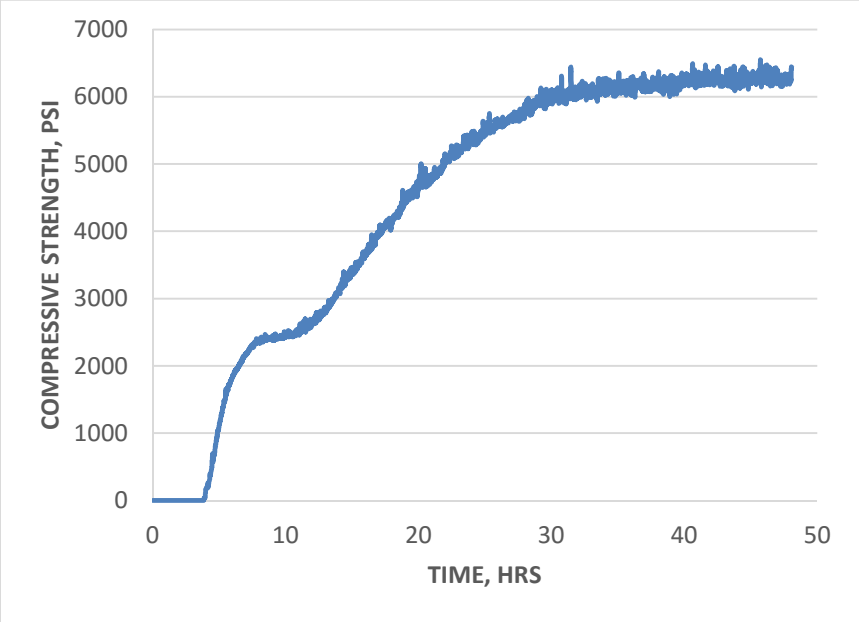

Figure 5-15: Compressive strength development of NZ2 slurry

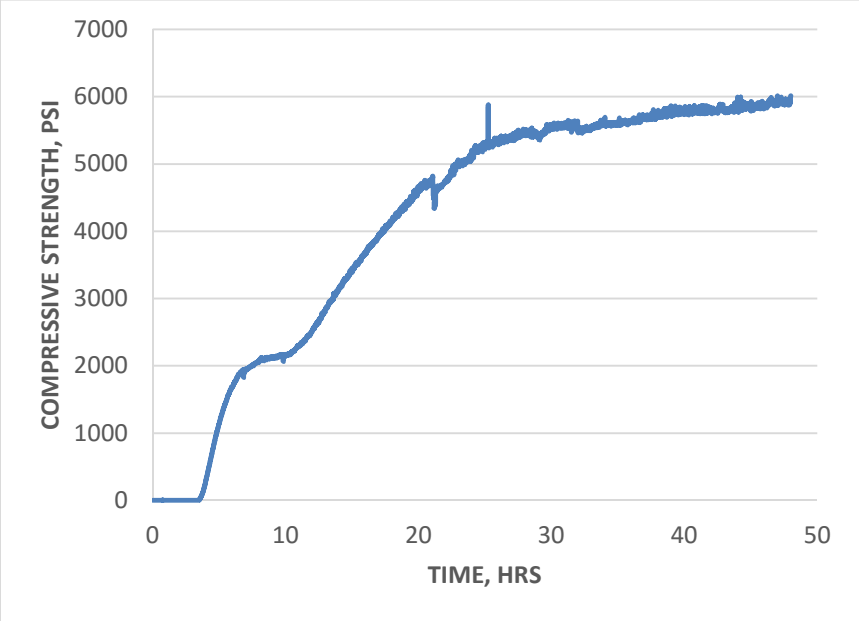

Figure 5-16: Compressive strength development of NZ3 slurry

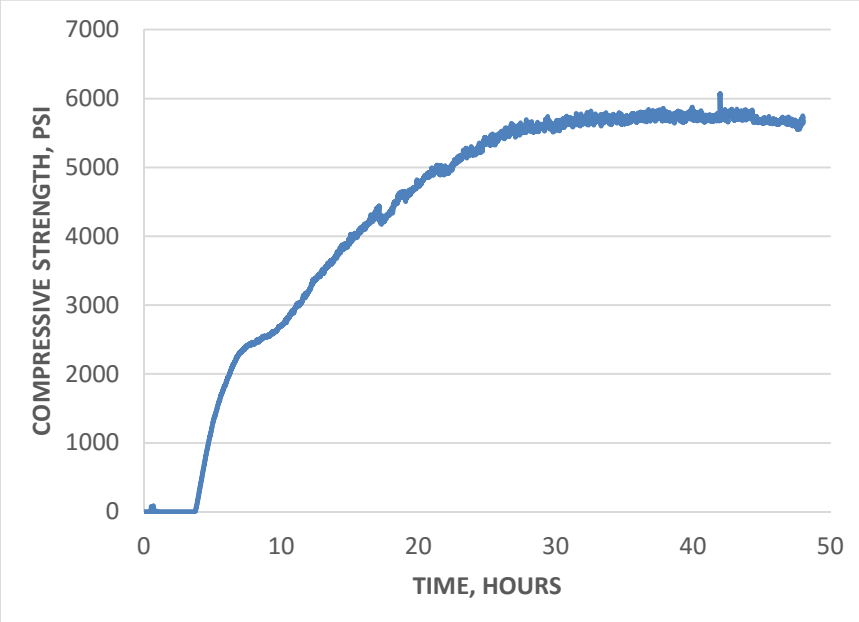

Figure 5-17: Compressive strength development of MZ1 slurry

Comparison of compressive development of base mix slurry and all mixes with Nano zeolite revealed that the effect of Nano zeolite on compressive strength was less significant in presence of all additives. At 24 hours, all Nano zeolite mixes have similar strength to base mix. At 48 hours, Nano zeolite 2% has higher compressive strength than all mixes. NZ2 has higher strength than other mixes at early time of 6 and 12 hours. MZ1 slurry on the other hand, has final strength at 48 hours lower than the base mix. However, the early compressive strength up to 12 hours is significantly higher. Comparison of compressive strength values of all the mixes at different time intervals are presented in **Figure 5-18** and **Table 5-7**.

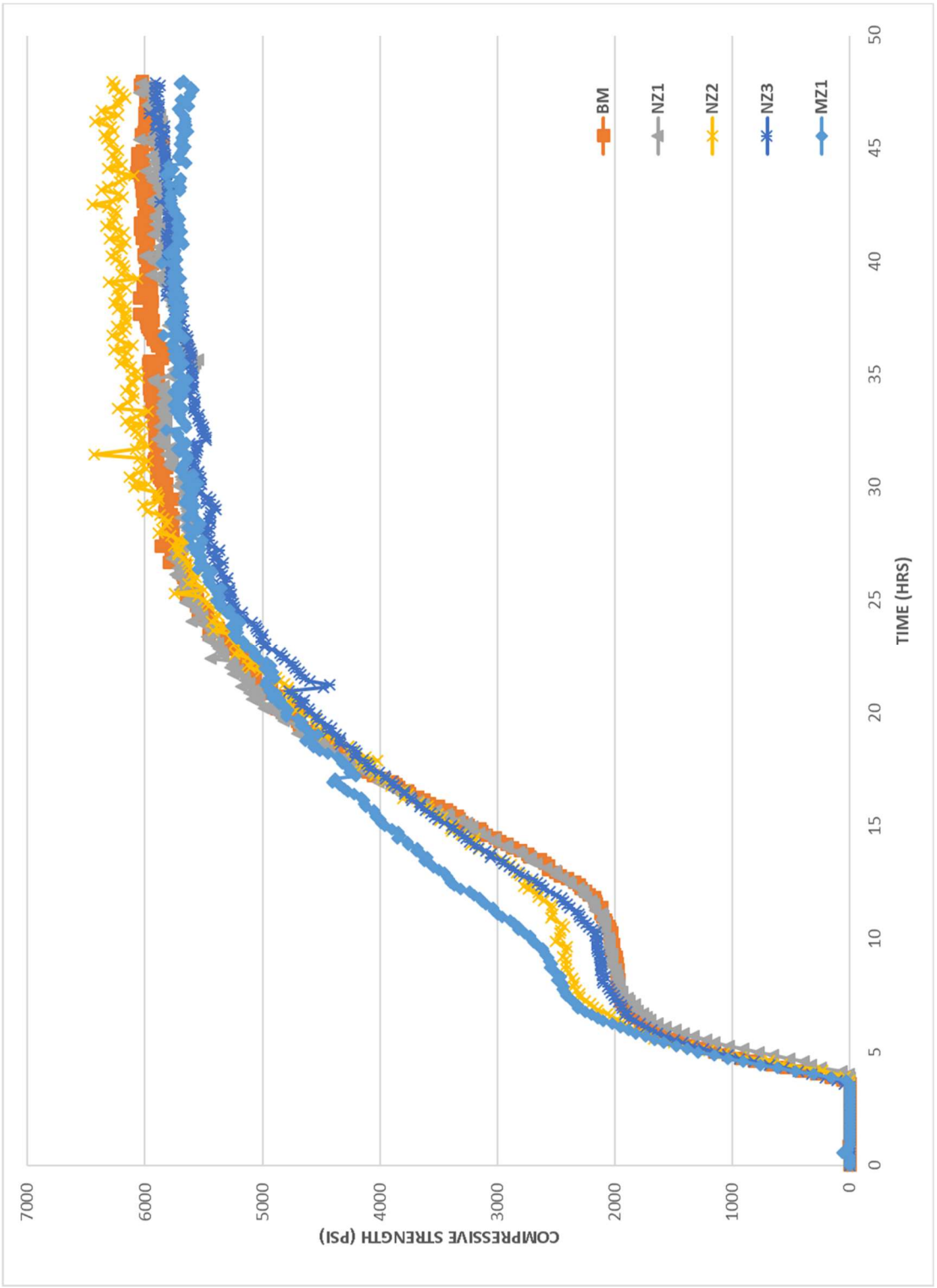

Figure 5-18: Comparison of strength development of base mix and zeolite slurries

Table 5-7: Compressive strength results at different time durations

Time (hh:mm)	BM (Psi)	NZ1 (Psi)	NZ2 (Psi)	NZ3 (Psi)	MZ1 (Psi)
06:00	1690	1500	1858	1693	1895
12:00	2223	2261	2685	2529	3199
18:00	4245	4342	4153	4143	4375
24:00	5434	5557	5435	5106	5219
48:00	6019	6007	6325	6013	5745

Time to achieve compressive strengths of 50, 500 and 2000 psi for slurries are summarized in **Table 5-8**, **Figure 5-19**, **Figure 5-20** and **Figure 5-21**. Time to reach a strength of 2000 psi is important as this strength is considered safe for perforation or stimulation job. It is observed Nano zeolite slurries have low time required to reach 2000 psi as compared to base mix. NZ2 slurry reached the 2000 psi strength in the shortest time. MZ2 slurry also reduced the time to achieve 2000 psi.

Table 5-8: Time to gain compressive strengths (50, 500 & 2000 psi)

Compressive Strength	BM	NZ1	NZ2	NZ3	MZ1
	Hours				
50 psi	3.73	4.12	3.94	3.62	3.77
500 psi	4.25	4.7	4.44	4.22	4.2
2000 psi	9.35	8.75	6.45	7.58	6.22

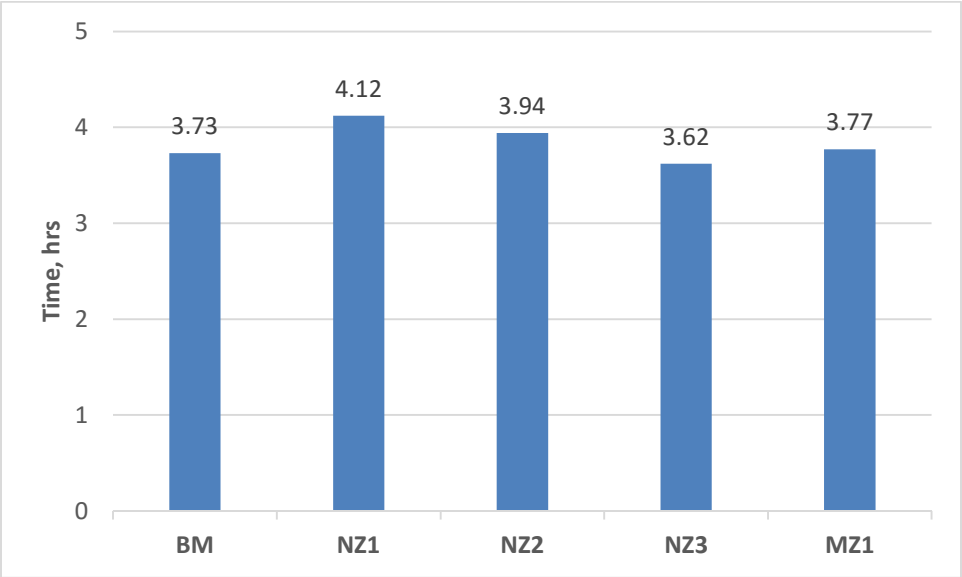

Figure 5-19: Time to gain 50 psi compressive strength

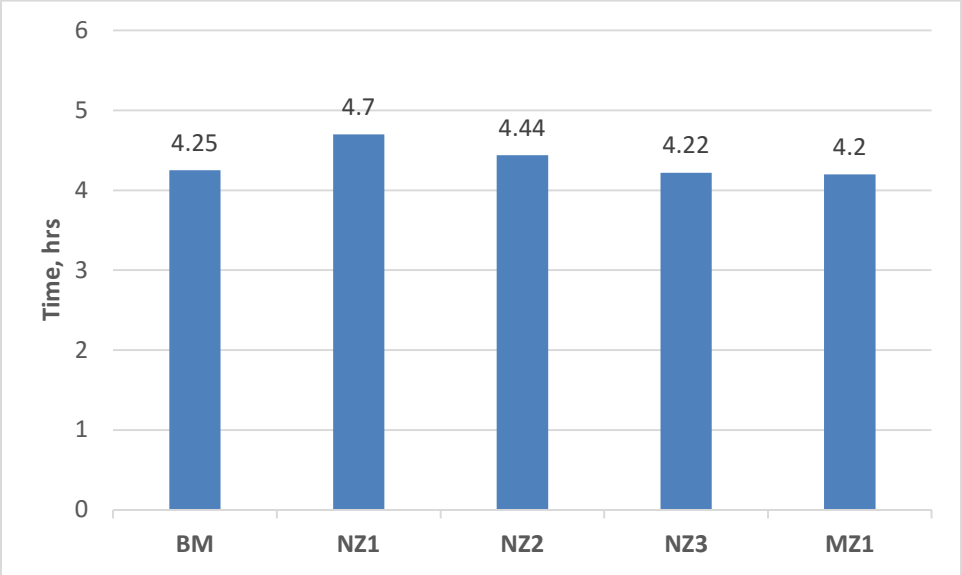

Figure 5-20: Time to gain 500 psi compressive strength

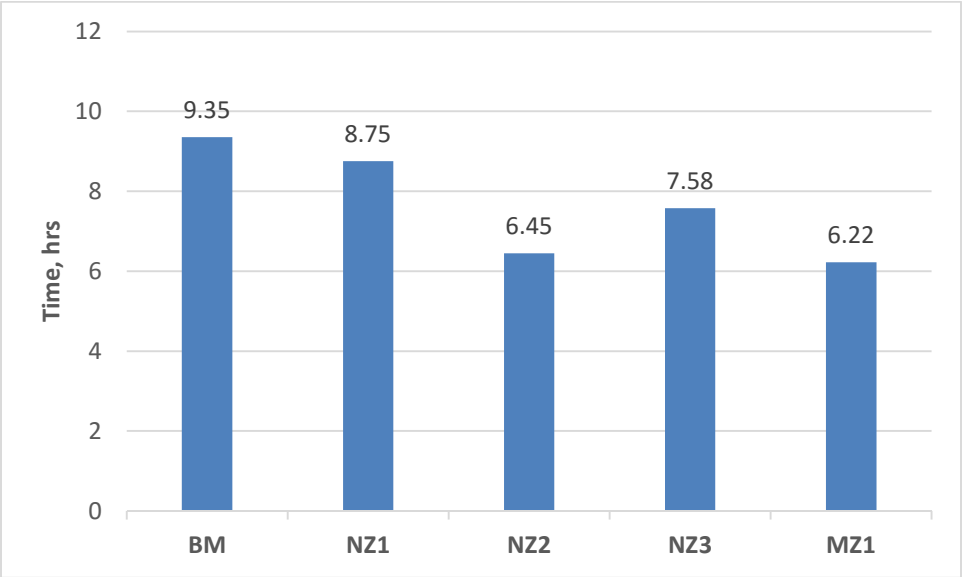

Figure 5-21: Time to gain 2000 psi compressive strength

Figure 5-22 presented the effect of Nano zeolite and micro zeolite on transition time from 50 psi to 500 psi. Increase in Nano zeolite concertation does not affect transition time significantly. On the contrary, micro zeolite reduced the transition time with small concentration.

5.6.2 Effect of Nano Zeolite on Destructive Compressive Strength

Unconfined compressive strength (UCS) is the maximum load per unit surface area a cement specimen can take before failing in a compression test with no confining pressure. For UCS, cement cubes are cured inside molds at BHST of 290°F and pressure 3000 psi for 24 hours. The cured cubes are crushed in Uniaxial strength testing equipment. Results of UCS tests for base mix and Nano zeolite slurries are presented in **Figure 5-23**. It is

observed that increase in amount of Nano zeolite increases the compressive strength. 1% Nano zeolite slurry showed a slight decrease in compressive strength.

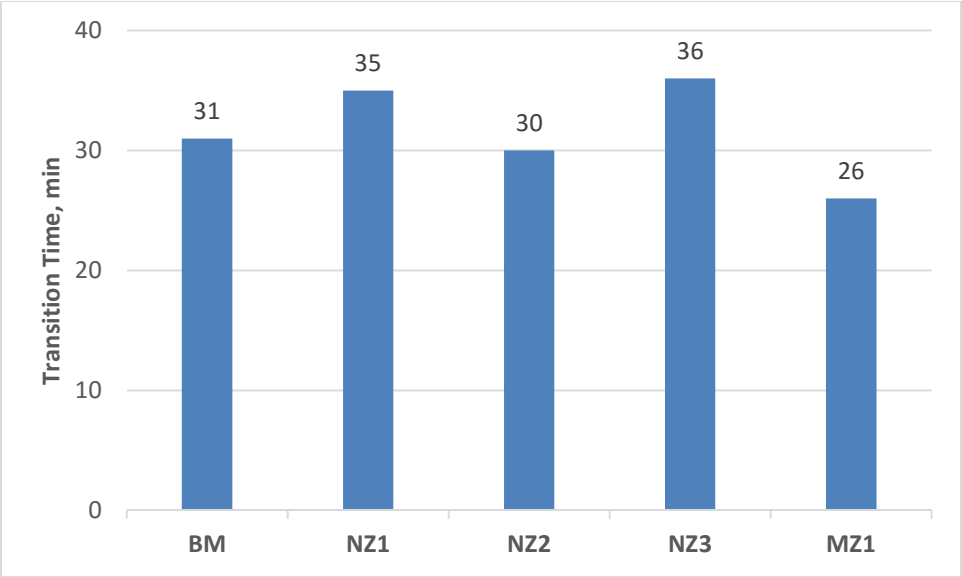

Figure 5-22: Transition time from 50psi to 500psi

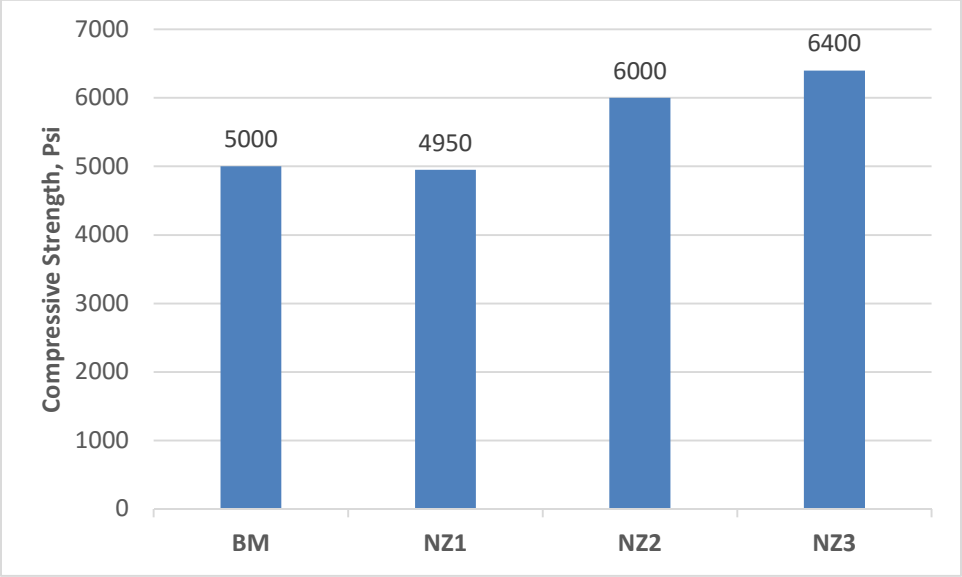

Figure 5-23: Compressive strength variation with Nano zeolite by crushing method

Young's modulus results are shown in **Figure 5-24** which indicates the increase of Young's modulus with the addition of Nano zeolite. Higher Young's modulus means stiffer set cement samples.

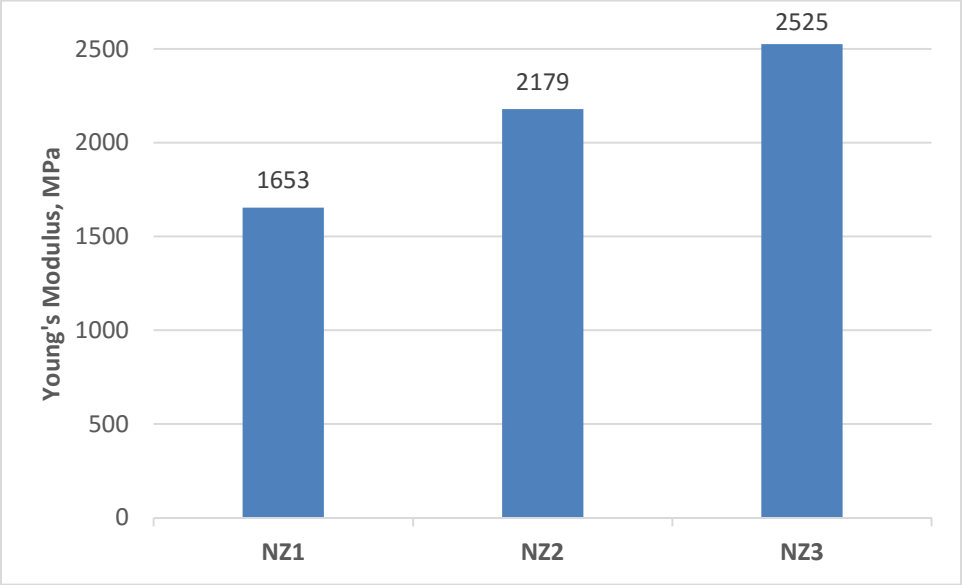

Figure 5-24: Young's Modulus Variation with addition of Nano zeolite

5.7 EFFECT OF NANO ZEOLITE ON TENSILE STRENGTH

Results of tensile strength calculated by Splitting Tensile Strength (STS) test for base mix and Nano zeolite slurries are given in **Figure 5-25** and **Table 5-9**. There was no specific trend with the increase in concentration of Nano zeolite. Tensile strength of Nano zeolite increased with 1% addition of Nano zeolite but then decreased with 2% Nano zeolite concentration. 3% tensile strength was similar to the 1% Nano zeolite slurry.

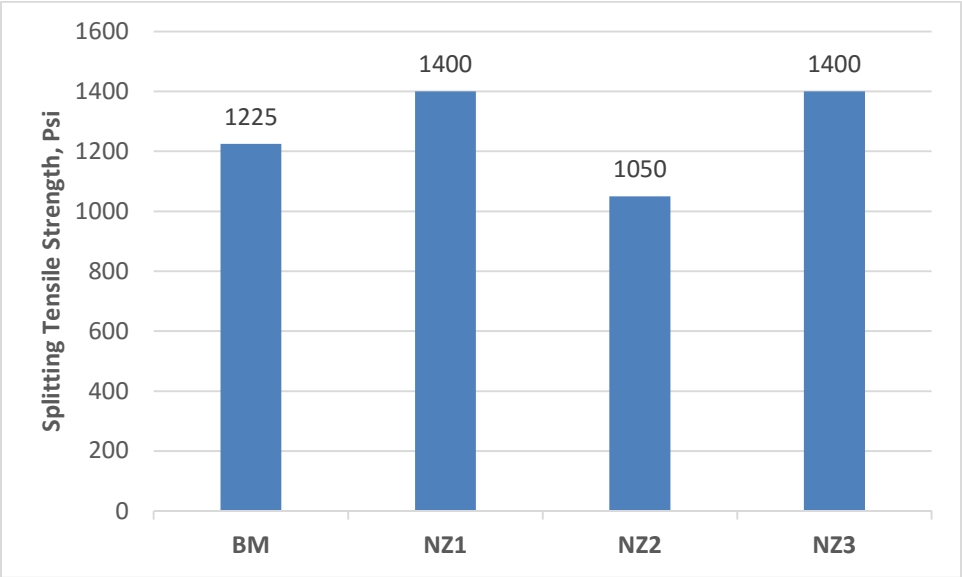

Figure 5-25: Splitting tensile strength trend with the addition of Nano zeolite

Table 5-9: Effect of Nano zeolite on Splitting tensile strength of all base mixes

Sample	BM (Psi)	NZ1 (Psi)	NZ2 (Psi)	NZ3 (Psi)
1	1100	1450	800*	850*
2	1350	1350	1050	1400
Average	1225	1400	1050	1400

* Rejected samples because of bad fracture

Results of splitting tensile strength are then converted to get uniaxial tensile strength, which are presented in **Table 5-10** and **Figure 5-26**.

Table 5-10: Conversion of Splitting tensile strength to uniaxial tensile strength (after Heinold et al 2003)

Tensile Strength	BM (Psi)	NZ1 (Psi)	NZ2 (Psi)	NZ3 (Psi)
STS	1225	1400	1050	1400
UTS	700	800	600	800

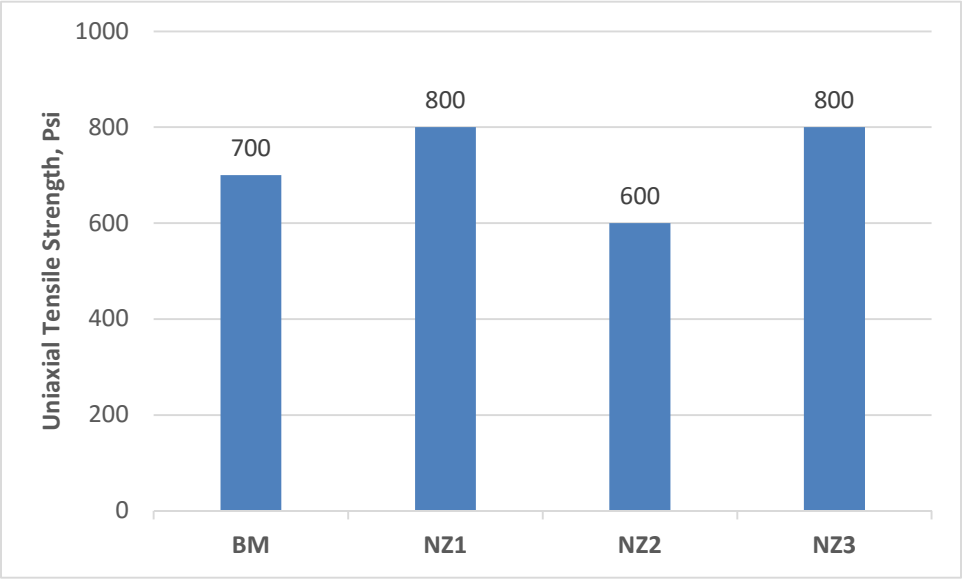

Figure 5-26: Effect of Nano zeolite on uniaxial tensile strength of all base mixes

5.8 EFFECT OF NANO ZEOLITE ON STATIC FLUID LOSS

Cement slurry fluid loss is another important property to determine how much fluid is lost when the slurry is exposed to a differential pressure. This could occur when cementing across high permeability zones, deep liners, or sensitive formations. Fluid loss was analyzed in non-stirring static fluid loss cell at temperature 190°F and pressure 1000 psi. Effect of Nano zeolite on fluid loss is summarized in **Table 5-11**. Measured fluid loss

of the slurries is less than 50 cc/30min which is good in case of both liner cementing and horizontal well cementing. The measured fluid loss was also good for preventing gas channeling as recommended by Al-Yami 2015.

Table 5-11: Fluid loss of base mix and Nano zeolite slurries

Properties	BM	NZ1	NZ2	NZ3
API fluid loss (cc/30min)	32	40	30	40

5.9 EFFECT OF NANO ZEOLITE ON POROSITY AND PERMEABILITY

Addition of Nano zeolite decreased the porosity and permeability of base mix slurry as shown in **Table 5-12** and **Figure 5-27**, **Figure 5-28**. Although, the base mix cement slurry had very low permeability, the addition of Nano zeolite further reduced the permeability. 1% Nano zeolite addition decreased the porosity slightly but further increase in Nano zeolite concentration increased the porosity.

Table 5-12: Effect of Nano zeolite on Porosity & Permeability of base mix slurry

Properties	BM	NZ1	NZ2
Porosity	21.57	20.51	23.35
Permeability (md)	0.0009	0.0005	0.0004

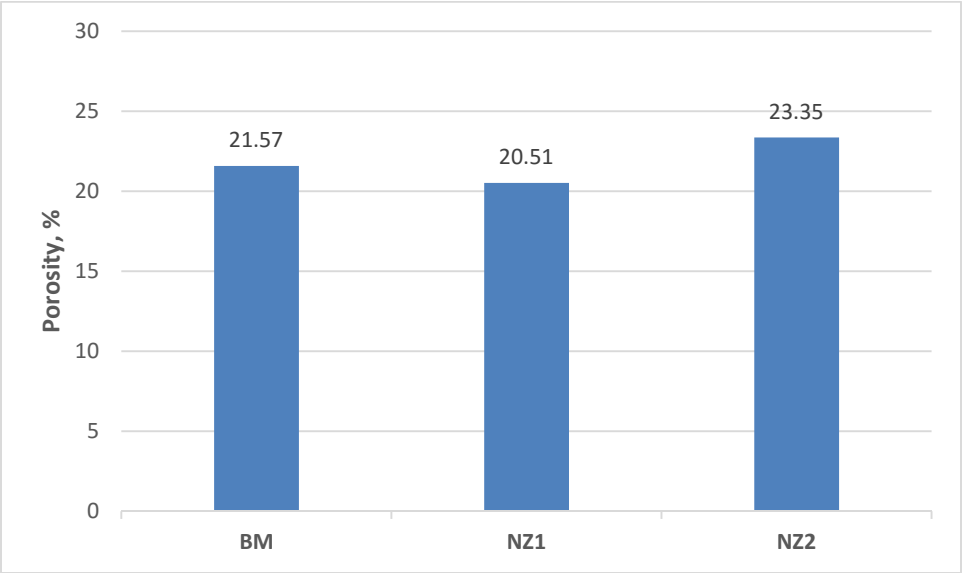

Figure 5-27: Porosity of base mix slurries with Nano zeolite

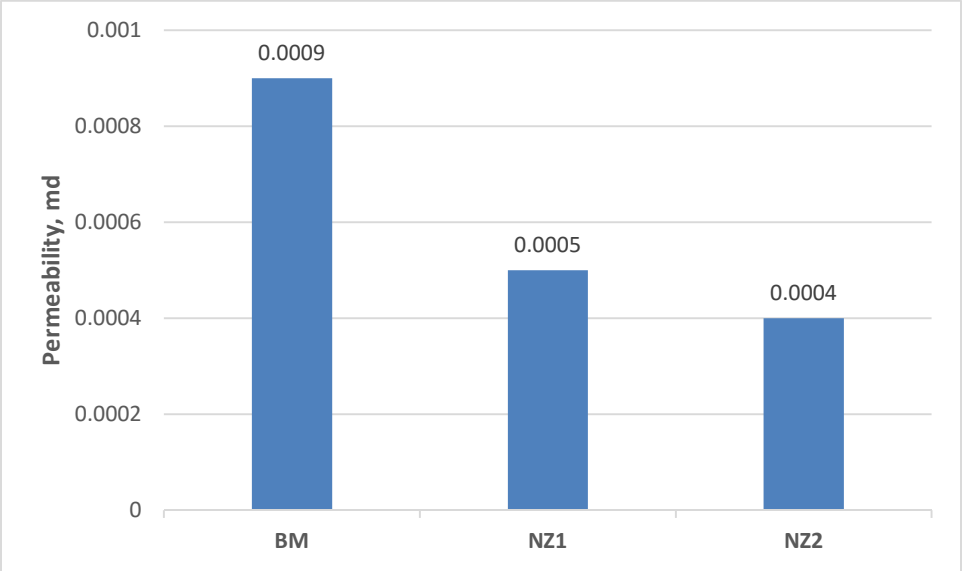

Figure 5-28: Permeability of base mix slurries with Nano zeolite

5.10 MICROSTRUCTURAL ANALYSIS

SEM and EDS analysis of BM slurry is shown in **Figure 5-29** and **Figure 5-30**.

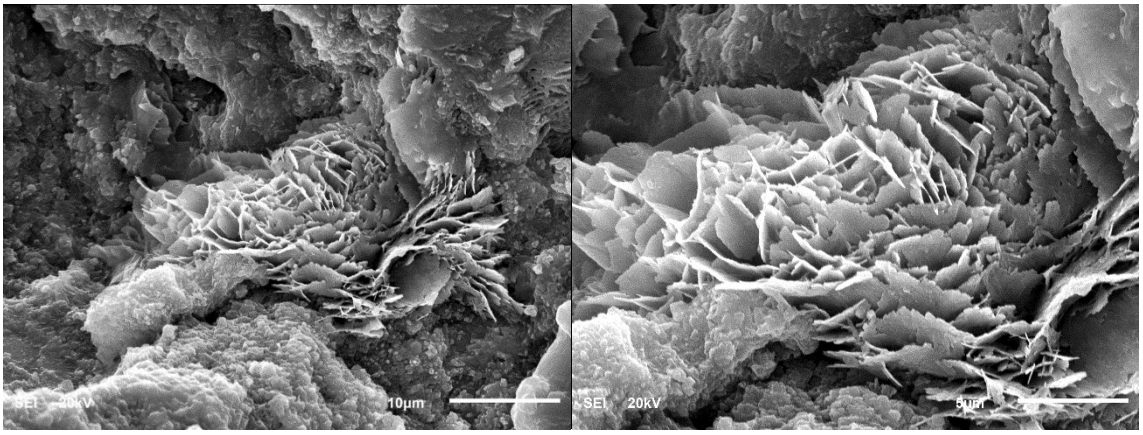

Figure 5-29: SEM images of set BM mix cured at 290°F for 24 hours

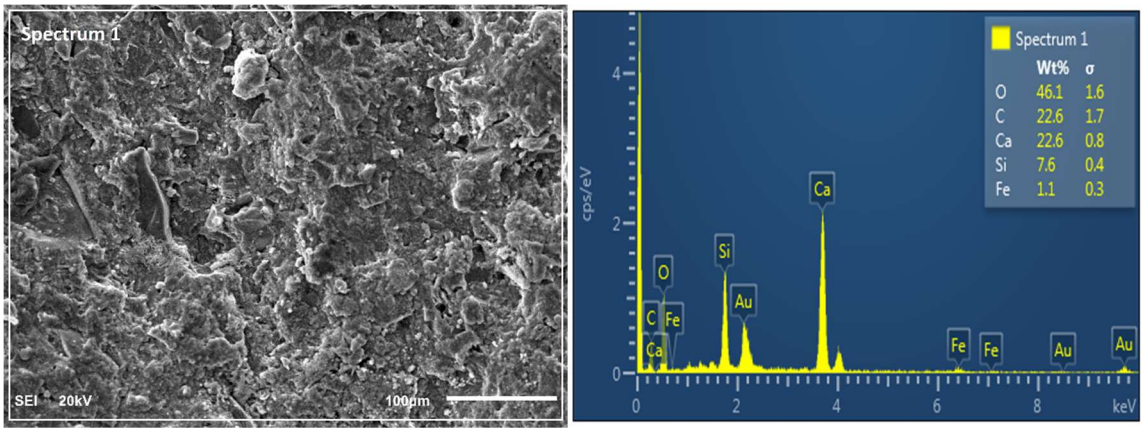

Figure 5-30: EDS results from BM mix

Dense and compact CSH can be observed in the image. Main difference between the BM slurries and G slurries is the silica flour. 35% Silica flour modified the hydration products and a denser microstructure is observed. A distinct structure is seen which can be

attributed to the Tobermorite. At high temperature CSH converts to Tobermorite in presence of silica. C/S ratio of 1.95 is obtained for the BM mix by EDS analysis.

SEM and EDS analysis of NZ1 slurry is shown in **Figure 5-31** and **Figure 5-32**. Crystalline form CSH can be observed in the images below. EDS analysis confirming the presence of CSH and C/S ratio of 2.6 is obtained for the NZ1 mix by EDS.

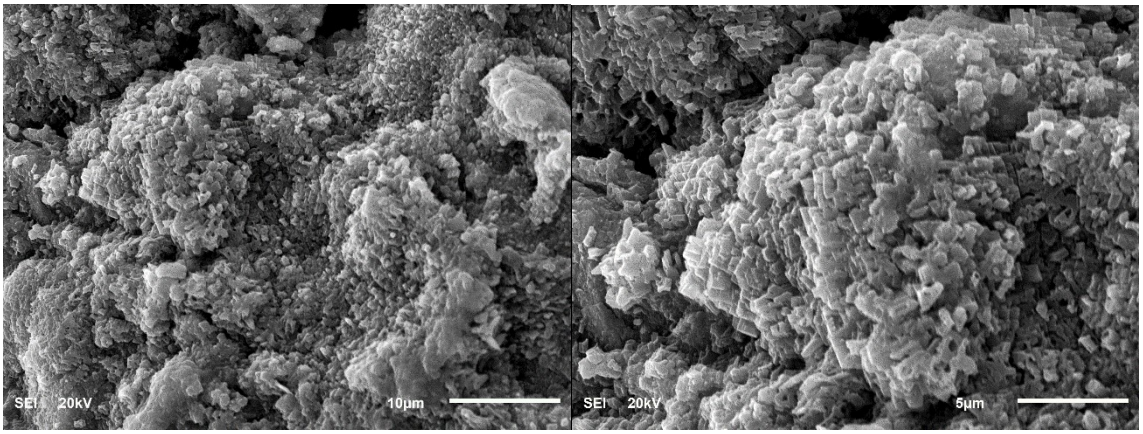

Figure 5-31: SEM image of set NZ1 mix cured at 290°F for 24 hours

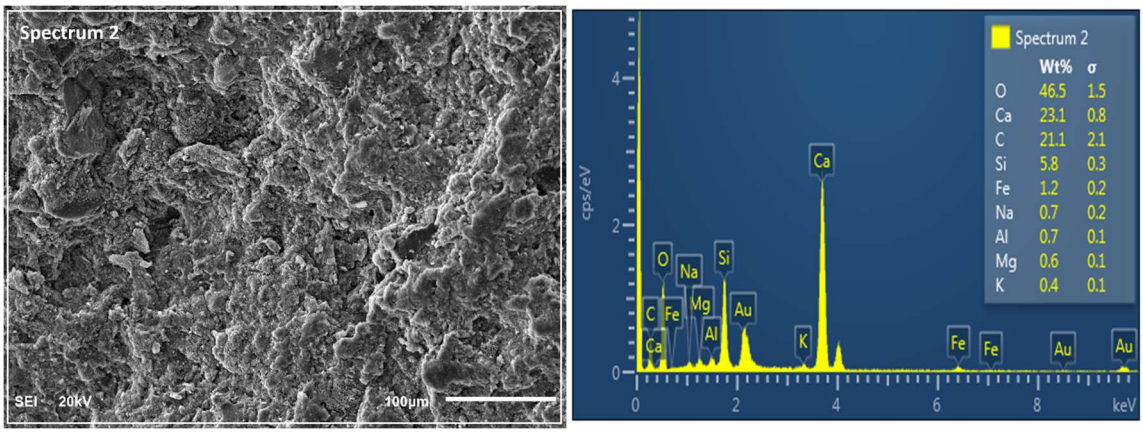

Figure 5-32: EDS results from NZ1 mix

SEM and EDS analysis of NZ2 slurry is shown in **Figure 5-33** and **Figure 5-34**. NZ2 mix appeared to be the densest of all the mixes. This observation is validated by the result of compressive strength, which showed highest compressive strength in NZ2 mix. In addition, permeability of the NZ2 mix is lowest among all mixes. EDS analysis confirming the presence of CSH with lowest C/S ratio of 1.2 which indicates a good form of CSH for avoiding strength retrogression.

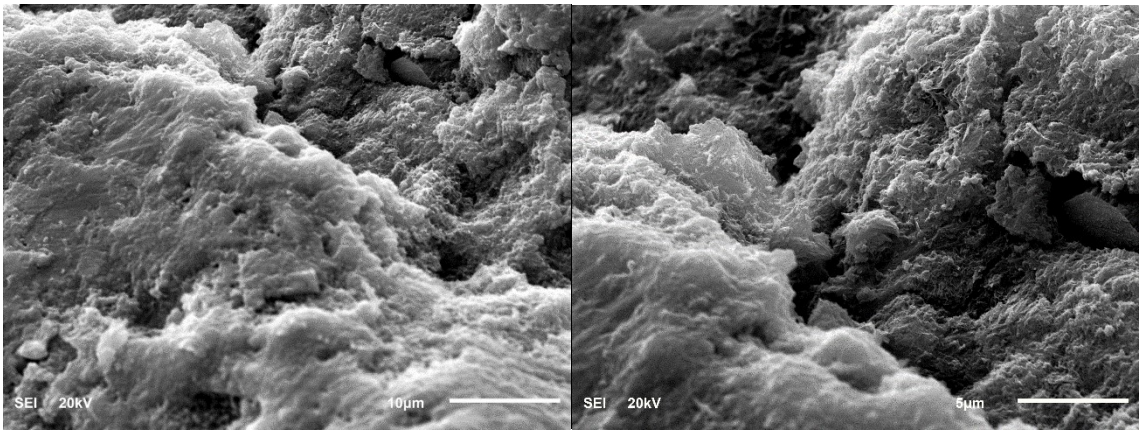

Figure 5-33: SEM image of set NZ2 mix cured at 290°F for 24 hours

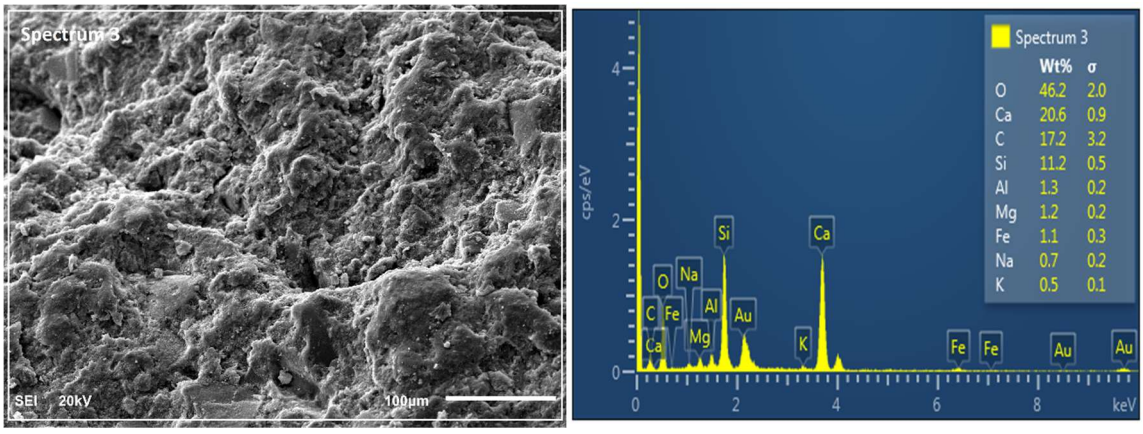

Figure 5-34: EDS results from NZ2 mix

SEM and EDS analysis of NZ3 mix is shown in **Figure 5-35** and **Figure 5-36**. **Figure 5-35** shows the SEM image from two different locations. The typical structure seen in BM is more evidently present in the NZ3 mix. Compressive strength result data for BM mixes showed similar strength in case of BM and NZ3. EDS analysis confirming the presence of CSH with C/S ratio of 1.9 which is close to the C/S ratio of BM.

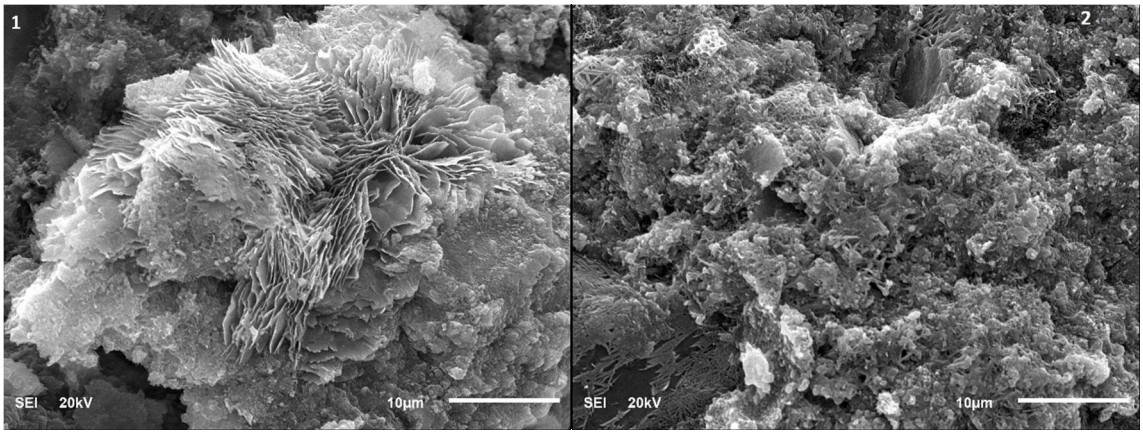

Figure 5-35: SEM image of set NZ3 mix cured at 290°F for 24 hours at 2 different points

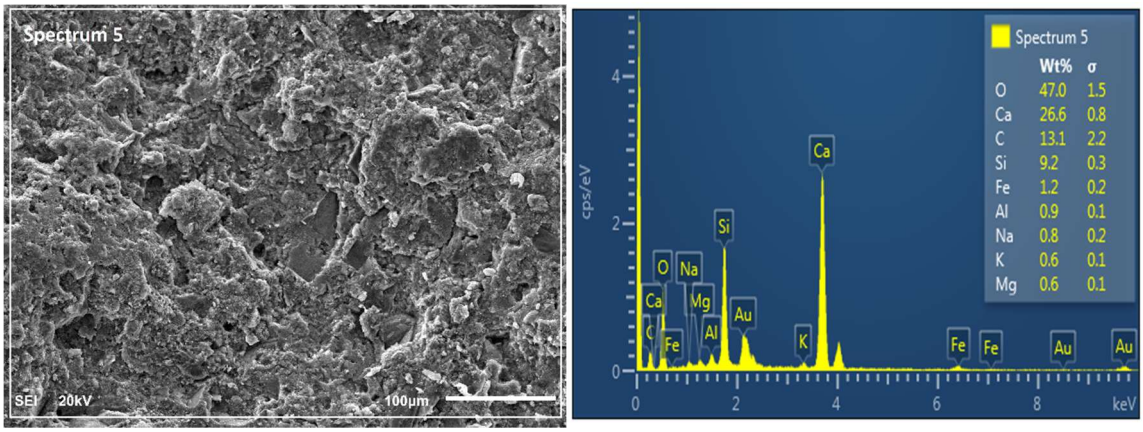

Figure 5-36: EDS results of Spectrum 5 from NZ3 mix

Overall, CSH gel is seen to be spread in the mix with two distinct surface textures, which are captured by Spectrum 6 and Spectrum 7 in EDS. EDS analysis for these two spectrums are presented in **Figure 5-37** and **Figure 5-38**. Spectrum 6 appears to be rich in calcium (C/S ratio = 4.15), while, spectrum 7 appears to be with higher silica content (C/S ratio = 2.74).

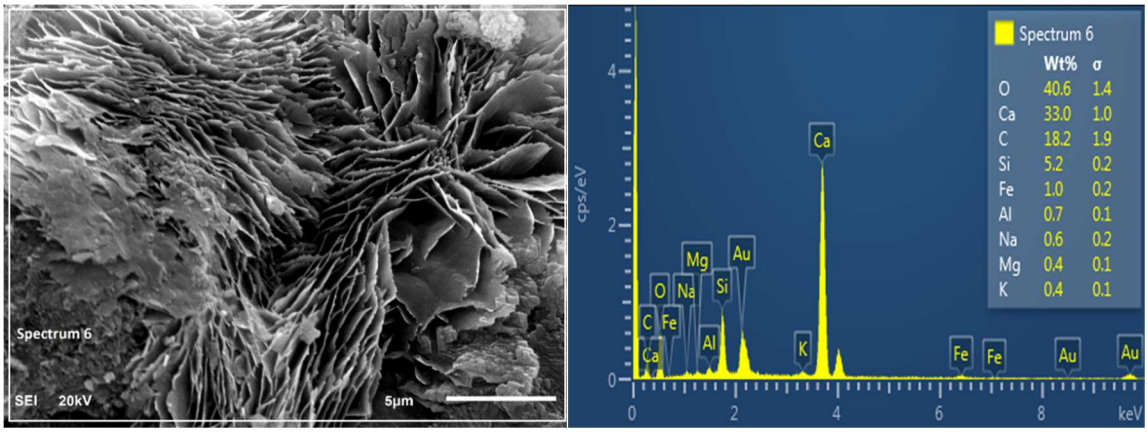

Figure 5-37: SEM image and EDS of NZ3 mix magnified at Point 1

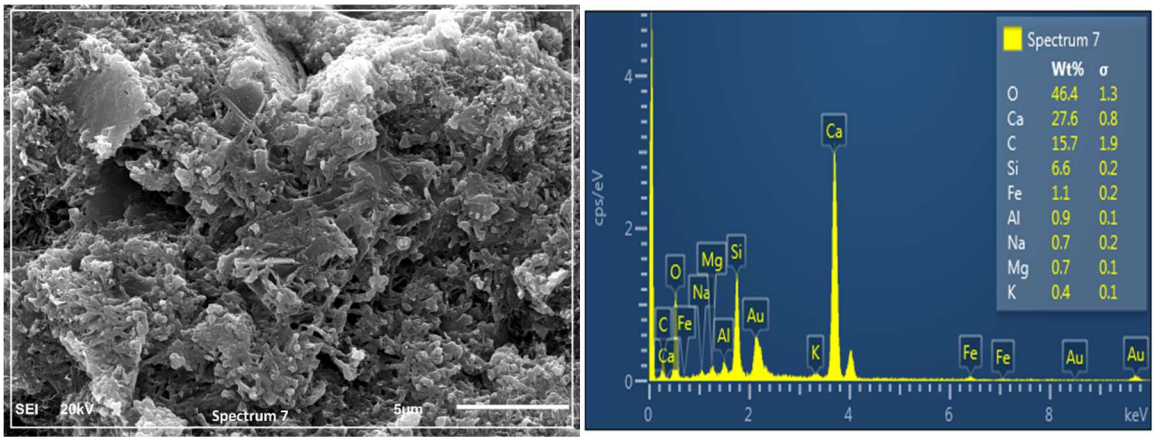

Figure 5-38: SEM image and EDS of NZ3 mix magnified at Point 2

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

This thesis is directed to assess the effect of Nano zeolite and micro zeolite on Portland Saudi cement type 'G' in high pressure and temperature cementing applications. Tests required to characterize the performance of cement with Zeolites have been conducted under HPHT conditions. Thickening time, free water separation, slurry density, rheological properties, compressive strengths, tensile strength, fluid loss and porosity and permeability tests have been conducted. The results of this study are restricted to the selected well conditions, cement used, chemical additives, percentages of Nano and micro zeolite, and cement slurry preparation and testing procedures. This study would be useful for researchers interested in this area and would provide valuable information for the enhancement of state of the art in cement with nanomaterials.

6.1 CONCLUSIONS

The findings of this investigation highlight the prospect of Zeolites in well cementing. Conclusions made from the study can be divided in two parts:

1. Experimental investigations of Nano zeolite with Class G cement.
2. Experimental investigations of Nano and micro zeolite with Class G cement and additives.

6.1.1 Experimental investigations of Nano zeolite with Class G cement

Conclusions made from this part of research are summarized as follows:

1. Rheological properties like plastic viscosity, yield point and gel strength of Class-G cement were increased.
2. Almost 30% reduction in time to reach 2000 psi was observed with 2% Nano zeolite addition.
3. Significant reduction of almost 98% and 17% in permeability and porosity respectively, was noticed with 1% addition of Nano zeolite.
4. From the microstructural analysis, it is obvious that small particles of Nano zeolite fill the pores and block the capillaries in the cement. As a result, they provide the dense microstructure which is evident from SEM images.
5. SEM images confirmed that Nano zeolite acts as a nano-filler in the cement matrix. Also, the cement hydration products were modified with the addition of Nano zeolite indicating Nano zeolite provided nucleation sites for growth CSH gel.

6.1.2 Experimental investigations of Nano and micro zeolite with Class G cement and additives

Conclusions made from this part of research are summarized as follows:

1) From thickening time test, it is observed that Nano zeolite has slight retardation effect on the setting of cement. On the other hand, micro zeolite acts as an accelerator as it increases the hydration reaction.
2) There is no free water separation in all zeolite cement systems after aging.
3) Both Nano and micro zeolite has minimal effect on the density of cement slurry.
4) It is investigated that both Nano and micro zeolite increase the plastic viscosity and yield point of cement slurry. This behavior can be beneficial in high temperature wells to avoid thermal thinning.
5) From the compressive strength by sonic method, it was observed that addition of Nano zeolite by 2% BWOC resulted in high early compressive strength. Also, micro zeolite with 1% addition resulted in higher early strength. Final strength is almost like the base mix slurries with both Nano zeolite and micro zeolite. 31% and 33% reduction in time to reach 2000 psi was observed with 2% Nano zeolite and 1% micro zeolite addition respectively.
6) From the compressive strength by destructive method, it was examined that addition of Nano zeolite increased the compressive strength except for 1% Nano zeolite which reduced it slightly. 3% BWOC NZ resulted in highest compressive strength.
7) Smaller addition of Nano zeolite increased the tensile strength, but tensile strength was decreased when concentration of Nano zeolite was increased further.

8) No significant effect on fluid loss of cement slurries by Nano zeolite is seen which can be attributed to the presence of different fluid loss additives in base mix slurry.
9) From the permeability and porosity investigations, it can be concluded that Nano zeolite addition decreases permeability and porosity. This indicates the nano-filler effect of Nano zeolite filling the pore spaces and thus reducing the permeability.

6.2 RECOMMENDATIONS

This work includes the findings of Nano zeolite and micro zeolite effects on oil-well cement properties in high pressure and temperature applications but still a lot of work left to be done. As both zeolites are enhancing the early compressive strength, the impact of zeolites with low pressure and temperature should also be investigated for shallow applications as accelerator.

Nano zeolite effects can also be investigated with different water to cement ratios and at different temperature and pressure conditions. Effect of micro zeolite should be investigated with neat cement slurry without additives. Effective dispersion of Nano zeolite in slurry appears to be a major hurdle to get the maximum benefit of Nano zeolite. In addition, Nano zeolite does not appear to be as reactive as it was expected, which can be attributed to its crystalline nature. Process of calcination, as suggested by literature to convert crystalline zeolite in amorphous form, should be investigated to increase the reactivity of Nano zeolite.

LIST OF ABBREVIATIONS

API	American Petroleum Institute
ASTM	American Standards for Testing and Measurement
BC	Bearden Consistency Unit
BHCT	Bottomhole Circulating Temperature
BHP	Bottomhole Pressure
BHST	Bottomhole Static Temperature
BWOC	By Weight of Cement
BWOW	By Weight of Water
CSH	Calcium Silicate Hydrate
HPHT	High Pressure High Temperature
HSR	High Sulphate Resistant
ISO	International Organization for Standardization
MSR	Moderate Sulphate Resistant
MW	Mud Weight
MZ	Micro zeolite
NZ	Nano zeolite
OSR	Ordinary Sulphate Resistant
OWC	Oil Well Cement
PCF	Pound per Cubic Feet
PV	Plastic Viscosity
RPM	Rotation per Minute
SEM	Scanning Electron Microscope
STS	Split Tensile Strength
TEM	Transmission Electron Microscopy
TRB	Time to Reach Bottom
TVD	Total Vertical Depth
UCA	Ultrasonic Cement Analyzer

UCS	Unconfined compressive strength
WOC	Wait on Cement
XRD	X-ray Diffraction
YP	Yield Point

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